Annex XV report

PROPOSAL FOR IDENTIFICATION OF A SUBSTANCE AS A CMR CAT 1 OR 2, PBT, vPvB OR A SUBSTANCE OF AN EQUIVALENT LEVEL OF CONCERN

Substance Name: **Chromium trioxide**

EC Number: **215-607-8;**

CAS number: **1333-82-0;**

Submitted by: Germany

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PROPOSAL FOR IDENTIFICATION OF A SUBSTANCE AS A CMR CAT 1 OR 2, PBT, VPVB OR A SUBSTANCE OF AN EQUIVALENT LEVEL OF CONCERN

Substance Name:	**Chromium trioxide**
EC Number:	**215-607-8;**
CAS number:	**1333-82-0;**

- *The substance is proposed to be identified as substance meeting the criteria of Article 57(a) and (b) of Regulation (EC) 1907/2006 (REACH) owing to its classification as carcinogen category 1 and mutagen category 2.*

Summary of how the substance meets the CMR (Cat 1 or 2), PBT or vPvB criteria, or is considered to be a substance of an equivalent level of concern

Chromium trioxide is covered by entry 024-001-00-0 in Annex VI, part 3, Table 3.2 (list of harmonised classification and labelling of hazardous substances from Annex I to Directive 67/548/EEC) of Regulation (EC) No 1272/2008 and listed as carcinogen, category 1 and mutagen, category 2[1].

Therefore, this classification of the substance in Regulation (EC) No 1272/2008 shows that it meets the criteria for classification as carcinogenic and mutagenic in accordance with Articles 57 (a) and 57 (b) of REACH.

Registration number(s) of the substance or of substances containing the substance:

The dissolution of chromium trioxide leads to an equilibrium between chromium trioxide, chromic acid, dichromic acid and oligomers of the mentioned acids as reaction products with water. As chromium trioxide is mainly used as a solution in water, another Annex XV dossier is specifically addressing the acids generated from chromium trioxide and their oligomers.

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[1] This corresponds to a classification as carcinogen (1A) and mutagen (1B) in Annex VI, part 3, Table 3.1 of Regulation (EC) No. 1272/2008 (list of harmonised classification and labelling of hazardous substances)

JUSTIFICATION

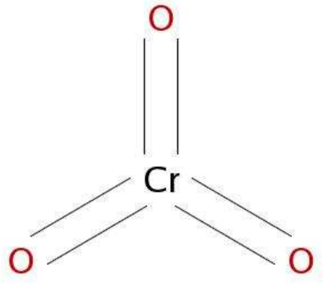
1 IDENTITY OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

1.1 Name and other identifiers of the substance

Chemical Name:	Chromium trioxide (CrO_3)
EC Name:	Chromium trioxide
CAS Number:	1333-82-0
IUPAC Name:	Trioxochromium

1.2 Composition of the substance

Chemical Name:	Chromium trioxide (CrO_3)
EC Number:	215-607-8
CAS Number:	1333-82-0
IUPAC Name:	Trioxochromium
Molecular Formula:	CrO_3
Structural Formula:	

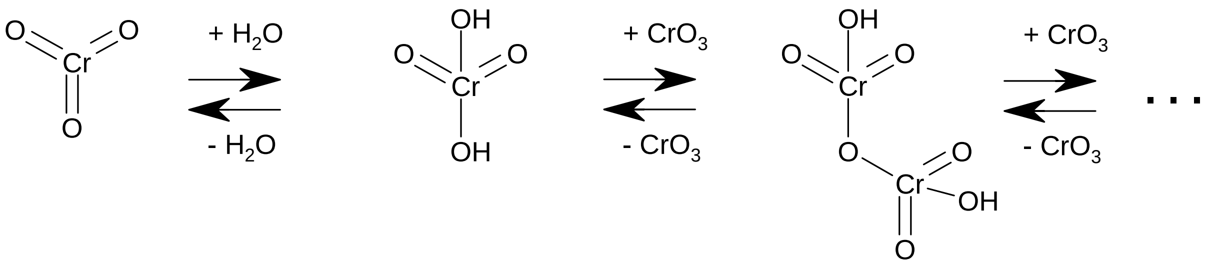


Molecular Weight:	99.99 g/mol
Typical concentration (% w/w):	Minimum > 98 %w/w
Concentration range (% w/w):	confidential

The dissolution of chromium trioxide in water leads to an equilibrium between chromium trioxide and chromic acid as a reaction product with water (Figure 1). Depending on the concentration of chromium trioxide and the pH-value the chemical equilibrium can be shifted towards dichromic acid or higher homologues.

Another Annex XV dossier covers specifically the acids generated from chromium trioxide and their oligomers.

Figure 1: Equilibrium of Chromium trioxide and its corresponding acids in water



1.3 Physico-chemical properties [2]

Table 1: Summary of physico-chemical properties

REACH ref Annex, §	Property	IUCLID section	Value	Reference
VII, 7.1	Physical state at 20°C and 101.3 kPa	4.1	solid	Merck, 1983
VII, 7.2	Melting/freezing point	4.2	196 °C	EC, 2005
VII, 7.3	Boiling point	4.3	n/a decomposes at ~250°C to Cr_2O_3 and O_2	EC, 2005
VII, 7.5	Vapour pressure	4.6	n/a inorganic ionic compound	EC, 2005
VII, 7.7	Water solubility	4.8	~1667 g/l at 20°C (a 1% solution has a pH<1)	EC, 2005
VII, 7.8	Partition coefficient n-octanol/water (log value)	4.7	n/a inorganic ionic compound	EC, 2005
XI, 7.16	Dissociation constant	4.21	---	
VII, 7.4	Relative Density	4.4	~2.7	EC, 2005

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[2] "Physico-chemical parameters such as boiling point, octanol-water partition coefficient and vapour pressure have little meaning for solid ionic inorganic compounds such as (....) chromates. The melting and decomposition characteristics of these compounds are well known and can be accessed in literature dating back to the 19th century. The most pertinent parameters are the high water solubility and the strong oxidising properties in acidic solutions to organic materials, particularly in the case of chromium trioxide." [EC, 2005]

2 HARMONISED CLASSIFICATION AND LABELLING

Chromium trioxide is covered by Index number 024-001-00-0 in Annex VI, part 3 of Regulation (EC) No 1272/2008 as follows:

Table 2: Classification according to part 3 of Annex VI, Table 3.2 (list of harmonized classification and labelling of hazardous substances from Annex I of Council Directive 67/548/EEC) of Regulation (EC) No 1272/2008

Index No	International Chemical Identification	EC No	CAS No	Classification	Labelling	Concentration Limits	Notes
024-001-00-0	chromium (VI) trioxide	215-607-8	1333-82-0	O; R9 Carc. Cat. 1; R45 Muta. Cat. 2; R46 Repr. Cat. 3; R62 T+; R26 T; R24/25-48/23 C; R35 R42/43 N; R50-53	O; T+; N R: 45-46-9-24/25-26-35-42/43-48/23-62-50/53 S: 53-45-60-61	C: R35: C ≥ 10 % C; R34: 5 % ≤ C < 10 % Xi; R36/37/38: 1 % ≤ C < 5 %	E

Table 3: Classification according to part 3 of Annex VI, Table 3.1 ((list of harmonised classification and labelling of hazardous substances) of Regulation (EC) No 1272/2008

Index No	International Chemical Identification	EC No	CAS No	Classification		Labelling			Spec. Conc. Limits, M-factors	Notes
				Hazard Class and Category Code(s)	Hazard statement code(s)	Pictogram, Signal Word Code(s)	Hazard statement code(s)	Suppl. Hazard statement code(s)		
024-001-00-0	chromium (VI) trioxide	215-607-8	1333-82-0	Ox. Sol. 1 Carc. 1A Muta. 1B Repr. 2 Acute Tox. 2 * Acute Tox. 3 * Acute Tox. 3 * STOT RE 1 Skin Corr. 1A Resp. Sens. 1 Skin Sens. 1 Aquatic Acute 1 Aquatic Chronic 1	H271 H350 H340 H361f *** H330 H311 H301 H372 ** H314 H334 H317 H400 H410	GHS03 GHS06 GHS08 GHS05 GHS09 Dgr	H271 H350 H340 H361f *** H330 H311 H301 H372 ** H314 H334 H317 H410		STOT SE 3; H335: C ≥ 1 %	

* explanation see chapter 1.2.1 of Annex VI of regulation 1272/2008 EC

** explanation see chapter 1.2.2 of Annex VI of regulation 1272/2008 EC

*** explanation see chapter 1.2.3 of Annex VI of regulation 1272/2008 EC

3 ENVIRONMENTAL FATE PROPERTIES

Not relevant for this dossier.

4 HUMAN HEALTH HAZARD ASSESSMENT

Chromium trioxide shows various toxicological properties like acute and chronic toxicity, corrosivity as well as skin and respiratory sensitisation. Furthermore chromium trioxide is a reproductive toxicant, a germ cell toxicant and in particular, a carcinogenic substance.

Health effects of soluble hexavalent chromium compounds have been reviewed in the Risk Assessment Report on chromium trioxide, sodium dichromate, sodium chromate, ammonium dichromate and potassium dichromate [EC 2005] which is mainly based on reviews from Cross et al. [1997] and Fairhurst and Minty [1989]. Furthermore comprehensive information including more recent studies has been presented by IARC [1990], ATSDR [2000], US EPA [1998a, 1998b], NIOSH [2008], Hartwig [2010] and the French annex XV draft dossiers on sodium chromate, potassium chromate, potassium dichromate and ammonium chromate [France, 2010a-d].

5 ENVIRONMENTAL HAZARD ASSESSMENT

Not relevant for this dossier.

6 CONCLUSIONS ON THE SVHC PROPERTIES

6.1 PBT, vPvB assessment

Not relevant for this dossier.

6.2 CMR assessment

Chromium trioxide is covered by entry 024-001-00-0 in Annex VI, part 3, Table 3.2 (list of harmonised classification and labelling of hazardous substances from Annex I to Directive 67/548/EEC) of Regulation (EC) No 1272/2008 and listed as carcinogen, category 1 and mutagen, category 2[3].

Therefore, this classification of the substance in Regulation (EC) No 1272/2008 shows that it meets the criteria for classification as carcinogenic and mutagenic in accordance with Articles 57 (a) and 57 (b) of REACH.

6.3 Substances of equivalent level of concern assessment

Not relevant for this dossier.

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[3] This corresponds to a classification as carcinogen (1A) and mutagen (1B) in Annex VI, part 3, Table 3.1 of Regulation (EC) No. 1272/2008 (list of harmonised classification and labelling of hazardous substances)

PART II

INFORMATION ON USE, EXPOSURE, ALTERNATIVES AND RISKS

The dissolution of chromium trioxide leads to an equilibrium between chromium trioxide, chromic acid, dichromic acid and oligomers of the mentioned acids as reaction products with water. As chromium trioxide is mainly used as a solution in water, the information provided in Part II of this dossier does not only cover chromium trioxide but as well its dissolution products.

The dissolution of chromium trioxide leads to an equilibrium between chromium trioxide, chromic acid, dichromic acid and oligomers of the mentioned acids as reaction products with water. As chromium trioxide is mainly used as a solution in water, the information provided in Part II of this dossier does not only cover the acids generated from chromium trioxide and their oligomers, but as well their parent substance chromium trioxide.

1 INFORMATION ON MANUFACTURE, IMPORT/EXPORT AND USES - CONCLUSIONS ON EXPOSURE.

According to the information in the RAR [EC, 2005] the global production capacities for chromium trioxide have been estimated by industry to about 184 000 t/a. The EU annual production quantity for chromium trioxide in 1997 was estimated to approximately 32 000 t/a. Europe is a net exporter of chromium (III) and chromium (VI) products, but localised importing may occur from outside the EU. After taking into account these exports and imports, the amount of chromium trioxide used in the EU is estimated to be 17 000 t/a.

Corresponding to the Human Health Risk Reduction Strategy for chromates [HSE, 2007] since 1997 two EU manufacturers have ceased production and in 2004 there was only one EU producer of chromium trioxide (in the UK). The information available in 2004 indicated that the production volumes are lower than in 1997 [HSE, 2007]. More recent information about the only manufacturer in the EU indicated that in 2006 they ceased manufacturing chromium trioxide. It appears that companies wishing to use chromium trioxide, must use imported sources [France, 2010a; France, 2010c; HSE, 2007].

The main uses of chromium trioxide are

- metal finishing
  (for electroplating e. g. hard chrome plating, decorative or bright-chrome plating, conversion coatings, e.g. passivation of zinc, aluminium, cadmium and brass, pickling ➔ [CrO_3 solution])
- manufacture of wood preservation products
  (biocidal agent (not relevant for REACH); fixing agent in waterborne wood preservatives)

Ancillary/Other uses of chromium trioxide are:

- catalyst manufacture,
- chromium dioxide manufacture
- pigment manufacture

- manufacture of paints, varnishes and inks putty (anticorrosive , dye)
- oxidant in organic chemistry
- electronic component manufacturing (characterization of silicon wafers)
- production of polyethylene and other plastics (catalyst)
- metallurgy of nonferrous metals (elaboration of chromium metal)
- manufacture of soap, detergents and cleaning agents
- manufacture of other organic basic chemicals
- inorganic hardening agent layer of photosensitive galantine
- manufacture of jewellery (production of synthetic sapphire)

and there are some additional uses in research and development:

- hardening of microscopic preparation
- oxidizer (Jones reagent, Sarret reagent)

The quantitative apportionment of chromium trioxide in industrial chemical substances and mixtures is 75 % in metal treatment formulations, 15 % in wood protection formulations, and 10 % in other [DEFRA, 2005].

Information from the Swedish Product Register

The following non-confidential use categories (UC 62) have been communicated to the Swedish product register in the year 2008 for chromic acid (CAS-No. 7738-94-5) or chromium trioxide (CAS-No. 1333-82-0) in preparations [KEMI, 2010]:

- Other metal surface treatment agents,
- salt for galvanic baths,
- other galvano-technical agents,
- pickling agents for metals,
- non-electrolytic metal coatings,
- surface treatment products for non-metal not specified otherwise,
- electrolytes,
- water based paints with anti-corrosive effect for industrial use,
- water based paints with anti-corrosive effect for other use,
- raw material for glass and ceramic,
- other laboratory chemicals,
- other impregnation agents,
- wood preservatives.

Number of employees in the main uses:

Metal finishing covers a wide range of varied and complex processes carried out by industry and involve both chemical and physical processing. In the EU there are more than 18 300 installations known to carry out surface treatment of metals and plastics.
Approximately 440 000 people are employed in the European surface treatment industry, most of these in small or medium enterprises (SMEs) typically employing 10-80 people [HSE, 2007]. However not all of these installations will use Cr^{VI}. If it is assumed approximately 10 % use Cr^{VI} then there are approximately 2 000 installations employing 44 000 people across the EU.

In Germany approx. 45 000 employees are occupied in the metal finish industry, 38 000 of them in 1 500 SMEs [UBA, 2007].

In the wood treatment branch approx. 24 000 employees are working in approx. 800 plants in Germany [Institut Fresenius, 2001; Hebisch et al., 2009]. For Europe no actual data were available. In total 222 occupational diseases (including approx. 90 % of lung tumours) were registered in Germany during a period of 1984 to 2006 [Pesch et al., 2008].

Process descriptions of the main uses

Formulation of metal treatment products

Many, often small, companies throughout the EU make formulations for use in metal treatment. The actual number of workers is unknown. The process is essentially one of mixing components together into a product and then packaging. There are two basic mixing processes used; dry or liquid. Chromium trioxide is the most common Cr^{VI} compound used.

Main processes in metal finishing where chromium trioxide is used

Information from the environment RRS [DEFRA, 2005] indicates that the metal treatment sector is dominated by the chromium plating sector, a much smaller part of this sector is the use of Cr^{VI} in passivates.

Chromium trioxide use in the metal treatment industry can be split into three basic types:

A. ***electroplating*** - this involves the deposition of a metallic coating on the base material, includes decorative, hard/engineering and decorative or bright chromium plating and electrolytic chromium/chromium oxide coated steel (ECCS).

hard chrome plating
This is the direct deposition of thick chromium layers without interlayer. The workpieces have to be pre-treated carefully. In comparison with the bright chrome plating the hard chrome plating uses higher acid concentrations (appr. 1 %), a lower chromium trioxide concentration (240 to 280 g/L) and higher current densities (40-50 A/dm ^{2}). The bath temperature is in the range of 55-60 °C. The current yield is 30 % [BGFE, 2007].

Bright chrome plating **or decorative chrome** plating
By means of this type of surface coating predominantly thin layers are deposited. Bright chrome plating mainly involves electroplating nickel onto the object before plating the chromium (it also sometimes involves electroplating copper onto the object before plating the chromium). For the bright chrome plating preferably electrolytes with a concentration of 320-380 g/L chromium trioxide are used. The current densities are 10 to 15 A/dm ^{2}. The current yield is 10-20 %, the bath temperature is about 40 °C.

B. ***Conversion coatings*** – this involves chemical treatment of metallic surfaces to give a barrier layer of complex chromium compounds to enhance corrosion protection on various metals.

Appellations for the method are: chromate, chromating;
exception: anodising in case of aluminia

Examples are:

Chromate is a group of methods of surface engineering where a chromium-containing protective layer is provided. The result is an inorganic non-metallic protective coating. The most common function of the chromate is corrosion protection, but can also be used to produce a bonding ground for subsequent layers, as a starting guard (in silver), to reduce the sensitivity fingerprint or alteration of appearance (gloss, color). Chromating can be applied to aluminum, magnesium, silver, cadmium and zinc.

Great technical importance gained the chromate treatment of zinc. The chromate of zinc is carried out by immersion in a solution of chromic acid and various additives.

Chromate is carried out without the application of a voltage. The layer thicknesses are between about 0.01 and 1.25 microns. The metallic character of the surface remains completely intact. This layer is chromium (VI)-free or chromium (VI)-containing. This method has found excellent for its corrosion protection and its wide distribution efficiency.

. Anodising, where an electrolytic process is used to produce an oxide layer on the surface of aluminium and passivation; - it is understood that chromic acid is used for treatment of aluminium passivation [Defra 2005].

C. ***Pickling, brightening*** **–** This process may be part of the surface pre-treatment before another process, e.g. electroplating. Pickling is a short-time bating for activating metal surfaces. It is usually used as an intermediate after degreasing and before a galvanic treatment is performed. Brightening is used to remove scale, passive films, alkaline residues or oxide films from the metal surface by dipping the substrate into a solution of chromium trioxide Chromium trioxide is only applied for copper and zinc and their alloys. Brightening solutions may contain chromium trioxide at a concentration of up to 350 g/l [DEFRA, 2005].

Wood treatment manufacture

Producers of copper chrome arsenate (CCA) and other chromium containing wood preservatives may formulate a concentrated product that is then supplied to industrial timber treatment plants. These plants dilute the product with water to prepare the treatment solution used to impregnate the timber.
There are a number of EU companies manufacturing copper chrome arsenate wood preservation products, with approximately 150 workers being directly involved in the process [HSE, 2007].

Use of chromium trioxide as fixing agent in waterborne wood preservatives

Chromic acid (chromium trioxide) is regarded as an active substance in wood preservatives according to Directive 98/8/EC under specific conditions and must not be placed on the market as active substances in wood preservatives since September 2006. According to a working document from the 27th meeting of Member States Competent Authorities [European Commission, 2007], wood preservatives containing chromic acid (chromium trioxide) as a fixative should meet the following main requirements: In products containing chromic acid the active substance must be a copper compound. The mass ratio of chromium acid to copper (II) oxide must not exceed a ratio of 3 to 1 in products. In these cases chromic acid is not assessed as an active substance but as a fixative. As a consequence, chromium does not have to be listed in Annex I of the directive 98/8/EC, but have to be treated as substance of concern in formulated biocidal products. Since the use as a fixative in biocidal products is not covered by the Directive 98/8/EC the REACH Regulation (EC) No.1907/2006 is mandatory.

It is noted that other Cr^{VI} containing wood preservatives; copper chrome (CC), copper chrome boron (CCB) and copper chrome phosphate (CCP) are manufactured and used in the EU in the same way as CCA products which have been restricted by Commission Directive 2003/2/EC.

CCA products contain chromium trioxide and are supplied as concentrates (2-5 % w/v), powders, liquids or pastes, which are diluted with water prior to use. According to the above mentioned requirements for use of chromic acid in wood preservatives, CCA and other products have to be applied by vacuum pressure impregnation. In this process Cr^{VI} is reduced to Cr^{III}. Inhalation exposures are likely to be highest when the wood is removed from the treatment vessel at the end of the cycle. Dermal exposure can occur at a number of stages in the process, particularly when unloading treated wood, during maintenance of the treatment vessel and from contact with contaminated surfaces.

A more detailed description of some uses is given in Annex XV Dossier Sodium Chromate [France, 2010d].

2 INFORMATION ON EXPOSURE

WORKER EXPOSURE

From 2007, coatings containing hexavalent chromium will no longer be permitted under the End of Life Vehicles Directive (Directive 2000/53/EC), [EC, 2000] and the EU-Directive RoHS (Restriction of the use of certain hazardous substances in electrical and electronic equipment), (Directive 2002/95/EC) [EC, 2002]. This will impact on some of the passivation applications where Cr^{VI} is present in the finished articles and substitution will become a necessity.

In addition, migration limits have been established within Council Directive 2009/48/EC [EC, 2009], for the presence of chromium (VI) in children's toys.

Considering that chromium compounds are no more manufactured in Europe [France, 2010a-d], workers exposure related to the manufacturing of chromium (VI) compounds is not expected.

Summarized description of the potential exposure

Production of dry and liquid metal treatment formulations can give rise to both inhalation and dermal exposures during weighing and mixing of ingredients and during packing of the final product.

Inhalation and dermal exposure can occur during weighing, mixing of the ingredients and during weighing and charging of reactants to vessels.

The development of gas (hydrogen) during the electroplating process leads to a discharge of aerosol from chromate electrolyte which is causing the risk of inhalative intake of Cr^{VI}.

Suppressants are used to reduce mist formation. During hard chrome plating related to a high hydrogen evolution, and consequently a greater discharge of chromic acid aerosols in the workplace air [BG/BGIA, 2006] as during the decorative - / bright chrome plating. In case of decorative chrome plating the hydrogen and thus the discharge of chromic acid aerosols in the air at the workplace is for process reasons not as pronounced as in hard chrome plating.

Such a mist is not formed during passive treatment so inhalation exposure in this process can be very low. However, although the concentration of an electrolytic solution (ca 12 - 26 % Cr^{VI}) is much greater than for passivates (≤ 1 % Cr^{VI}), passivate solutions need to be made up regularly (sometimes daily) when there is potential for exposure to the 50 % passivate concentrate. Electrolytic solutions last longer, but also require regular top up of solution.

Inhalation and dermal exposure can also occur in all types of process when:

- chromate solutions are made up and added to the treatment bath;
- from drag out and splashing; and
- when re-threading treated workpieces

In the wood treatment manufacture exposure can occur during weighing and mixing of reactants and during packing of the finished product.

In the wood preservation industry the risk of inhalative and dermal exposure during the charging and discharging of the reactor is the main problem.

Summary of exposure data

The risk related to chromium (VI) compounds has been already assessed in the Risk Assessment Report (RAR) published in 2005 [EC, 2005] and which focused on chromium trioxide, sodium chromate, sodium dichromate, potassium dichromate and ammonium dichromate. All these substances (apparently with the exception of chromium trioxide) are included in the Candidate List.

The five Cr^{VI} compounds all readily dissolve in aqueous environments in the body and the chromate/dichromate ions produced from all five compounds behave similarly in biological tissues and hence, other than the additional property of acidity and its potential influence on toxicity for chromium trioxide, the five can be treated as a common group.

There are a number of countries with exposure limits (as Cr^{VI}) for Chromium (VI) or chromium compounds and these have been tabulated in the RAR [EC, 2005].

The occupational exposure limits listed in the RAR only relate to inhalation exposure. Occupational exposure limits are not usually set for dermal exposure.

For information, the Occupational Safety and Health Administration (OSHA) proposed to tighten the standard for hexavalent chromium occupational exposure with a permissible exposure limit (PEL) value for chromium (VI) of 0.005 mg/m^3 (calculated as an 8-hour time-weighted average (TWA)) [OSHA, 2008].

In Germany the occupational exposure limit, which was based on the technical feasibility (TRK) was withdrawn in 2006.

INHALATION EXPOSURE

First it should be given a summary of occupational inhalation exposure data from the Risk Assessment Report [EC, 2005]

Inhalation exposure data as summarised in the RAR are given in Tables 4 and 5.

Table 4: Summary of the inhalation exposure data of Cr^{VI} from RAR.

Industry	**Reasonable worst case ($\mu g/m^3$) as** Cr^{VI}	**Source**	**Number of samples**
manufacture of the 5 chromates	20	measured data	1,889
manufacture of other Cr containing chemicals			
- dyestuffs	500 (8 hr) 1,500 (short term)	measured data judgement	39
- chrome tan	7	measured data	115
- manufacture Cr metal	10	measured data	73
- formulation metal treatment products	20	measured data	25
Use in metal treatment			
- electrolytic	20	measured data	315
- passivation	1	measured data	42
manufacture of Montans wax	4	EASE	
manufacture of vitamin K	2.5	EASE	
use as a mordant in wool dyeing	500	measured data	3
catalyst manufacture	5	measured data	22

Table 5: Inhalation data supplied since completion of the RAR [HSE, 2007].

Industry	**Number of samples**	**Range of data ($\mu g/m^3$ Cr^{VI})**
manufacture of the 5 chromates	180	5 – 7
manufacture of other Cr containing chemicals		
- dyestuffs	4	2, 2.6 20, 52
- chrome tan	1	2
- manufacture Cr metal	2	<30, <20
- formulation metal treatment products	1	<0. 1
Use in metal treatment		
- electrolytic	34 8	10 – 20 (RWC - 0.005) < 0. 1 – 0. 6
- ECCS	>55	0. 2 – 10
- passivation	2	3, < 1
manufacture of Montans wax	2	5.5, < 3
manufacture of Vitamin K		
use as a mordant in wool dyeing	1	0. 3
catalyst manufacture	*	1 – 50 (total Cr)

Inhalation exposure data on manufacturing process are given only for information as chromium compounds are no more manufactured in Europe [France, 2010d].

In the RAR [EC, 2005] the Reasonable Worst-Case (RWC) inhalation exposures are based on the 90th percentile of available measured data with professional judgment used where limited data were available. EASE was used to predict exposures for two scenarios (manufacture of Montans Wax and Vitamin K) where little or no information was available.

DERMAL EXPOSURE

Table 6 shows the summary dermal exposure data from the RAR [EC, 2005]. With the exception of CCA use all are based on EASE predictions, as no measured dermal sampling data were available.

The data for CCA use, taken from the RRS [HSE, 2007] project show the amount of Cr^{VI} on the skin.

Table 6: Summary of the dermal exposure data from RAR.[4]

Industry	Range of exposures ($\mu g/cm^2$/day)	Source
Manufacture of the five chromates	0 – 100	EASE
Manufacture of other Cr containing chemicals - dyestuffs - chrome tan - manufacture Cr metal - formulation of metal treatment products	 100 – 1,000 0 – 100 very low 0 – 100/ 100 – 1,000	 EASE EASE EASE EASE
CCA use	1,370 – 41,710 mg Cr^{VI} on skin RWC – 16,500 mg Cr^{VI} on skin	Measured data
Use in metal treatment - mixing of solutions - adding to bath - drag out - re-threading steel strip	 0 – 100 0 – 100 1,000 – 5,000 100 – 1,000	EASE
manufacture of Montans wax	100 – 1,000	EASE
manufacture of Vitamin K	0 – 100	EASE
use as a mordant in wool dyeing	100 – 1,000	EASE
catalyst manufacture - unloading - process sampling	 0 – 0.1 very low / 0.1 – 1	EASE

Dermal exposure can occur at a number of stages in the wood treatment process, particularly when the bogie containing the treated wood is unloaded, during maintenance of the treatment vessel and from contact with contaminated surfaces. Exposures ranged from 1.37 - 41.71 mg Cr^{VI} on the skin. The RWC of 16.5 mg Cr^{VI} on the skin was based on the 90th percentile of the data.

No new dermal exposure data are available since the RAR was completed.

Exposure to chromium VI compounds (2000 - 2009) in Germany

Introduction

The German worker exposure data were provided by the IFA-Institute for Occupational Safety and Health of the German Social Accident Insurance.

The new data provided by the IFA were measured in industry for the years 2000 to 2009. The data are differentiated into personal sampling data taken while the individual was carrying out all activities, i.e. active plant work, control room work and break periods and data from static sampling in the different workplaces.
The identification and documentation of the following evaluated data from exposures in the workplace are based on the criteria of the MGU - measuring hazard identification of accident insurance carrier (formerly BGMG) [Gabriel, 2010]. A quality management system, which es-

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[4] The EASE dermal exposure estimations refer to the total amount of substance or solutions disposed on the skin [HSE, 1999].

sentially implements the requirements of DIN EN ISO 9001, is the standard of MGU secure. The testing laboratories are operated in accordance with DIN EN ISO 17025.

All data collected will be merged into the exposure database MEGA (measurement data to exposure to hazardous substances at work). The MEGA exposure database is maintained and evaluated for the institutions for statutory accident insurance and prevention by Institute for Occupational Safety and Health of the German Social Accident Insurance (IFA, formerly BGIA; German: Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung).

If individual measurements are below the limit of quantification (LOQ) of the applied analytical method, half of this value is taken into account within the statistical evaluation. The MEGAPRO software, developed by IFA, allows the statistical analysis of the data of the exposure database MEGA according to different selection criteria and evaluation strategies.

Criteria for the inclusion of data in the evaluation

- measurements related to exposure
- sampling duration ≥ 1 hour
- exposure time ≥ 6 hours

- data collectives, were **excluded** when:
  - consisting of less than 10 measurements or
  - data from less than three different German Social Accident Insurances or
  - data from less than five different companies[5]

To get a better comparability to the adapted risk based occupational exposure limits (see Table 22), the MEGA measurement data were converted into µg/m^3 by multiplying the original values, given in mg/m^3 by the factor 1000.

In case of few original data which had only two internal decimal places, the corresponding result of the multiplication showed a zero for the unit position. Therefore, in these rare cases the unit position of the µg/m^3 amount does not represent the exact result of the related analytical determination but is only the outcome of the computation.

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[5] Management agreement between the German Social Accident Insurances and the German Statutory Accident Insurance for the purpose of data protection.

Evaluation Strategy and selection criteria

Table 7– 19 show the evaluated German worker exposure data (expresses as Cr^{VI}) collected in the years 2000-2009.

The evaluation is made in the form of industry (branch groups) and work area groups and further differentiated by the sampling strategy (static or on the person) and the presence of a LEV (Local Exhaust Ventilation). A general overview of the branch groups, which are in correlation to the main uses mentioned at the beginning of chapter “Information on Manufacture and uses” is given in Table 7 to 10.

An overview on the occupational exposure in the major industry (branch) group (metal processing and engineering) including almost 80 % of the total measurement values is given in Table 11 to 14. A deeper analysis of the exposure of workers in the main work area group (surface treatment and electroplating) representing more than 35% of the whole data collective, separated into exposure relevant processes, is considered separately in the same way in the Tables 15 to 19.

Table 7: Overview Branch-Groups

Groups	Number of samples	Arithm. Mean	Arithm. Std. Dev.	Geom. Mean	Geom. Std. Dev.	50th-perc.	75th-perc.	90th-perc.	95th-perc.
		(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)
Total	3 755	14	137	2.43	4 928	LOQ (!)	2.7 (+)	15 (+)	35.2 (+)
Waste management and facility management	12	2.65	1.09	2.31	1 978	LOQ (!)	LOQ (!)	LOQ (!)	4.4 (+)
Construction industry	118	8.86	24.9	3.2	3 695	LOQ (!)	5.75 (+)	17.2	29.4
Education institute	12	5.21	12	1.64	4 196	LOQ (!)	2.5 (+)	4.5 (+)	20.2
Chemical industry	49	17.7	52.5	3.07	6 243	LOQ (!)	5.65 (+)	26.8 (+)	82.2
Electrical and optical equipment	156	6.32	15.8	2.98	2 705	LOQ (!)	LOQ (!)	10.4	21.4
Wood and paper	162	0.713	2.31	0.108	4 750	LOQ (!)	LOQ (!)	LOQ (!)	2.5 (+)
Ceramics	33	6.64	10.1	2.89	3 670	2.5 (+)	7.75	14.7	22.1
Plastics industry	24	7.88	15.8	1.59	7 586	LOQ (!)	5 (+)	18.8	43.6
Metal working and mechanical engineering	2 992	15.8	152	2.84	4 255	LOQ (!)	3.15 (+)	16	40
Metal production	117	9.56	40.1	1.7	6 142	LOQ (!)	2.5 (+)	12.3	23

Table 8: Overview Branch-Groups – personal and static

Groups		Number of samples	Arithm. Mean (µg/m³)	Arithm. Std. Dev. (µg/m³)	Geom. Mean (µg/m³)	Geom. Std. Dev. (µg/m³)	50th-perc. (µg/m³)	75th-perc. (µg/m³)	90th-perc. (µg/m³)	95th-perc. (µg/m³)
Total	personal	1 918	22	189	4.36	3 302	LOQ (!)	6 (+)	24.2 (+)	55.1
	static	1 837	5.64	28.2	1.32	5 617	LOQ (!)	2.5 (+)	7.03 (+)	18
Construction industry	personal	75	12.2	30.7	4.87	3 027	LOQ (!)	9.4	22.5	37.2
	static	43	3.09	3.91	1.54	3 730	LOQ (!)	2.5 (+)	7.55	11.5
Chemical industry	personal	33	25	62.9	5.41	4 694	LOQ (!)	12.7 (+)	35.4 (+)	134
	static	16	2.76	3.95	0.955	6 446	LOQ (!)	2.5 (+)	4.42 (+)	9.04
Electrical engineering, precision mechanics, optics	personal	93	5.92	13.1	3.4	2 166	LOQ (!)	LOQ (!)	11	16.4
	static	63	6.9	19.2	2.45	3 437	LOQ (!)	LOQ (!)	3.2 (+)	22.7
Wood and paper	static	154	0.621	2.33	0.0914	4 132	LOQ (!)	LOQ (!)	LOQ (!)	2.47 (+)
Plastics industry	personal	14	13	19.3	5.35	3 882	LOQ (!)	11.2	38.2	53.2
	static	10	0.716	0.85	0.291	4 620	LOQ (!)	1.22 (+)	1.5 (+)	2 (+)
Metal working and mechanical engineering	personal	1 585	24.1	207	4.37	3 364	LOQ (!)	6 (+)	25	62
	static	1 407	6.52	31.8	1.75	4 649	LOQ (!)	2.5 (+)	8.1	21
Metal production	personal	53	16.6	57	4.48	3 285	LOQ (!)	8 (+)	21.7	36.9
	static	64	3.77	13.9	0.757	6 395	LOQ (!)	2.5 (+)	4.2 (+)	7.2

Table 9: Overview Branch-Groups with LEV

Groups	Number of samples	Arithm. Mean	Arithm. Std. Dev.	Geom. Mean	Geom. Std. Dev.	50th-perc.	75th-perc.	90th-perc.	95th-perc.
		(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)
Total	2 463	11.6	58.7	2.65	4 771	LOQ (!)	4.1 (+)	16 (+)	39 (+)
Construction industry	36	10.9	19.8	4.7	3 281	LOQ (!)	9.3	19	50.6
Chemical industry	34	24.4	62.1	3.41	8 853	LOQ (!)	15.5 (+)	35.2 (+)	132
Electrical engineering, precision mechanics, optics	111	7.45	18.4	3.22	2 782	LOQ (!)	LOQ (!)	11.9	27.1
Wood and paper	81	0.554	1.34	0.108	4 622	LOQ (!)	LOQ (!)	LOQ (!)	LOQ (!)
Plastics industry	17	9.58	18	2.26	7 270	LOQ (!)	5.6 (+)	24.5	51.1
Metal working and mechanical engineering	2 033	12.5	63.8	3	4 161	LOQ (!)	4.58 (+)	17.7	41
Metal production	75	5.98	14.5	1.48	6 568	LOQ (!)	2.5 (+)	13.5	23

Table 10: Overview Branch-Groups without LEV

Groups	Number of samples	Arithm. Mean	Arithm. Std. Dev.	Geom. Mean	Geom. Std. Dev.	50th-perc.	75th-perc.	90th-perc.	95th-perc.
		(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)
Total	988	18	243	1.8	5 405	LOQ (!)	2.5 (+)	9.72 (+)	23.6
Construction industry	56	5.14	7.42	2.61	3 478	LOQ (!)	2.5 (+)	12.3	22.2
Chemical industry	11	2.81	1.56	2.47	1 703	LOQ (!)	LOQ (!)	LOQ (!)	5.28 (+)
Electrical engineering, precision mechanics, optics	39	3.68	4.65	2.45	2 647	LOQ (!)	LOQ (!)	4.39 (+)	11.3
Wood and paper	80	0.883	2.99	0.108	4 964	LOQ (!)	LOQ (!)	2.35 (+)	2.5 (+)
Metal working and mechanical engineering	733	22.9	282	2.32	4 485	LOQ (!)	2.5 (+)	11.7	28.8
Metal production	25	2.82	2.73	1.61	4 070	LOQ (!)	LOQ (!)	5.5	7.13

Table 11: Branch-Group - Metal working and mechanical engineering

Groups	Number of samples	Arithm. Mean	Arithm. Std. Dev.	Geom. Mean	Geom. Std. Dev.	50th-perc.	75th-perc.	90th-perc.	95th-perc.
		(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)
Plant manufacturing, steel construction and Light metal construction	160	12.7	33.7	3.74	4 530	LOQ (!)	8.3	28	52
Apparatus engineering	123	17.9	42.1	5.19	4 073	LOQ (!)	11	50	92.2
Vehicle construction	99	7	13.4	3.36	3 121	LOQ (!)	6.17 (+)	13.2	27.1
Galvanic	1 174	8.36	36.4	2.54	4 081	LOQ (!)	2.8 (+)	13	28
Machine-building and vehicle construction, generally	83	29.8	110	3.95	4 837	LOQ (!)	5.07 (+)	32.6	53.4
Machine-building	272	20.1	83.6	3.17	4 805	LOQ (!)	2.5 (+)	20.8	81.6
Metal working and mechanical engineering, generally	774	8.51	41.7	2.6	3 652	LOQ (!)	2.5 (+)	11	27.9
Surface finishing and hardening	100	6.13	9.79	2.83	3 550	LOQ (!)	5 (+)	14	26
Repair workshops	30	29.8	107	3.96	6 178	LOQ (!)	5.17 (+)	25	92
Liquid-coating	71	230	922	5.05	17 319	2.5 (+)	35	283	1,212

Table 12: Branch-Group - Metal working and mechanical engineering – personal and static

Groups		Number of samples	Arithm. Mean	Arithm. Std. Dev.	Geom. Mean	Geom. Std. Dev.	50th-perc.	75th-perc.	90th-perc.	95th-perc.
			($\mu g/m^3$)	($\mu g/m^3$)	($\mu g/m^3$)	($\mu g/m^3$)	($\mu g/m^3$)	($\mu g/m^3$)	($\mu g/m^3$)	($\mu g/m^3$)
Plant manufacturing, steel construction and Light metal construction	personal	103	16.6	40.7	5.68	3 380	LOQ (!)	9.4	35.1	60.5
	static	57	5.71	11.5	1.76	5 457	LOQ (!)	2.5 (+)	16.3	29.1
Apparatus engineering	personal	84	23.5	49	7.07	4 141	LOQ (!)	21	64.4	123
	static	39	5.88	14.8	2.66	3 061	LOQ (!)	4.47 (+)	6.67	11.5
Vehicle construction	personal	68	8.48	14.9	4.57	2 530	LOQ (!)	7	15.8	27.6
	static	31	3.76	8.31	1.71	3 572	LOQ (!)	2.5 (+)	2.86 (+)	9.83
Galvanic	personal	424	9.94	29.6	4.08	2 685	LOQ (!)	5.4 (+)	16.6	37.6
	static	750	7.47	39.7	1.95	4 630	LOQ (!)	2.5 (+)	9.2	21.5
Machine-building and vehicle construction, generally	personal	62	39.2	126	5.49	4 691	LOQ (!)	8.05	47.6	284
	static	21	2.21	1.29	1.49	3 498	LOQ (!)	LOQ (!)	2.5 (+)	4.59 (+)
Machine-building	personal	191	26.5	98	4.77	3 877	LOQ (!)	4.81 (+)	34.9	119
	static	81	5.11	22.4	1.21	5 099	LOQ (!)	2.5 (+)	4.94 (+)	12.7
Metal working and mechanical engineering, generally	personal	487	11.3	51.8	3.72	2 825	LOQ (!)	LOQ (!)	17	35.7
	static	287	3.75	9.83	1.42	4 280	LOQ (!)	2.5 (+)	3.63 (+)	9.72
Surface finishing and hardening	personal	52	6.38	10	3.7	2 455	LOQ (!)	5 (+)	13.8	25.4
	static	48	5.86	9.65	2.12	4 618	2.5 (+)	3.2 (+)	15.2	26.6
Repair workshops	personal	24	36.7	119	5.9	4 573	LOQ (!)	13	48.4	109
Liquid-coating	personal	21	735	1,609	66.3	16 392	110	573	1,840	1,995
	static	50	17.5	51.7	1.71	8 132	1 (!)	5.45	32.0	82

Table 13: Branch-Group - Metal working and mechanical engineering with LEV

Groups	Number of samples	Arithm. Mean	Arithm. Std. Dev.	Geom. Mean	Geom. Std. Dev.	50th-perc.	75th-perc.	90th-perc.	95th-perc.
		(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)
Plant manufacturing, steel construction and Light metal construction	88	13.6	35.5	3.56	5 224	LOQ (!)	8	29.2	58
Apparatus engineering	75	16.1	30.4	5.43	3 818	LOQ (!)	10.3	52.5	89.2
Vehicle construction	54	9.47	17.2	4.51	2 809	LOQ (!)	7.05	18.6	48.5
Galvanic	892	9.63	40.6	2.74	4 284	LOQ (!)	4.9 (+)	15	33.8
Machine-building and vehicle construction, generally	53	31.6	120	3.92	4 014	LOQ (!)	4.92 (+)	12.8	133
Machine-building	184	15.3	55.7	2.97	4 514	LOQ (!)	2.5 (+)	19	57.8
Metal working and construction, generally)	504	9.91	49.7	2.77	3 738	LOQ (!)	2.5 (+)	13	32.8
Surface finishing and hardening	77	7.37	10.8	3.64	3 315	LOQ (!)	6.22	24.3	27.3
Repair workshops	16	48.8	145	6.84	5 109	LOQ (!)	13	58.8	212
Liquid-coating	12	209	537	18	13 384	12	99	200	886

Table 14: Branch-Group - Metal working and mechanical engineering without LEV

Groups	Number of samples	Arithm. Mean	Arithm. Std. Dev.	Geom. Mean	Geom. Std. Dev.	50th-perc.	75th-perc.	90th-perc.	95th-perc.
		(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)
Plant manufactoring, steel construction and Light metal construction	59	8.34	16.4	3.54	3 635	LOQ (!)	5.65 (+)	24	33.1
Apparatus engineering	37	24.5	62.9	5.22	5 054	LOQ (!)	16.3	42.5	106
Vehicle construction	39	4.4	5.38	2.54	3 389	LOQ (!)	2.66 (+)	10.2	13.3
Galvanic	213	4.53	18.5	1.87	3 559	LOQ (!)	LOQ (!)	4.58 (+)	9.11
Machine-building and vehicle construction, generally	22	8.53	14.4	2.77	5 689	LOQ (!)	4.75 (+)	19.2	43.4
Machine-building	56	14.4	38.8	3.51	4 467	LOQ (!)	3 (+)	18.4	86
Metal working and mechanical engineering, generally	205	5.04	11.7	2.17	3 552	LOQ (!)	LOQ (!)	7.1 (+)	22.5
Surface finishing and hardening	21	1.91	2.03	1.14	3 229	LOQ (!)	2.5 (!)	2.5 (!)	3.16 (!)
Repair workshops	no data								

Table 15: Work-area-group - Surface treatment and electroplating

Groups	Number of sam-ples	Arithm. Mean	Arithm. Std. Dev.	Geom. Mean	Geom. Std. Dev.	50th-perc.	75th-perc.	90th-perc.	95th-perc.
		(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)
Surface treatment and electroplating	1 403	7.85	33.1	2.5	4 074	LOQ (!)	3 (+)	13	28
Surface treatment and electroplating (personal)	533	8.89	24.9	3.99	2 604	LOQ (!)	5.1 (+)	16	33.4
Surface treatment and electroplating (static)	870	7.21	37.2	1.88	4 720	LOQ (!)	2.5 (+)	9.2	22
Surface treatment and electroplating (with LEV)	1 083	9.24	37.4	2.77	4 211	LOQ (!)	5 (+)	15	32.8
Surface treatment and electroplating (without LEV)	250	3.08	6.95	1.63	3 586	LOQ (!)	LOQ (!)	2.8 (+)	7.65 (+)

Table 16: Work-area-group - Surface treatment and electroplating –differentiated into work processes

Work area	Number of samples	Arithm. Mean	Arithm. Std. Dev.	Geom. Mean	Geom. Std. Dev.	50th-perc.	75th-perc.	90th-perc.	95th-perc.
		(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)
Manual assembly	26	2.92	2.67	2.12	3 015	LOQ (!)	LOQ (!)	3.58 (+)	5.2
Plating, generally	147	5.7	17.9	1.96	4 342	LOQ (!)	2.5 (+)	8.56 (+)	16
Plating, decorative	31	3.7	4.8	2.55	2 090	LOQ (!)	LOQ (!)	3.94 (+)	15
Plating, decorative, sulphuric bath	45	5.07	16.3	1.79	3 913	LOQ (!)	2.5 (+)	4.6 (+)	7.97
Hard chrome plating	60	45.6	139	7.74	4 817	5 (+)	14	78	290
Hard chrome plating, mixed acid bath	43	11.3	19.6	4.15	5 284	3.25 (+)	11.5	27.4	31.4
Hard chrome plating, sulphuric bath	242	12.5	21.9	4.78	4 177	3.7 (+)	12	34.6	51.6
Plating, black	21	2.95	2.06	2.35	2 164	LOQ (!)	2.5 (+)	6.46	7.95
Chromium plating, generally	158	3.66	9.73	1.5	4 158	LOQ (!)	2.5 (+)	5.02 (+)	7.1
To chromize	72	5.33	20	2.04	3 429	LOQ (!)	LOQ (!)	3.94 (+)	9.4
Surface treatment, generally	44	5.39	7.16	1.81	6 038	2.5 (+)	8 (+)	14.6	18.8
Surface coating, galvanic processes	188	4.61	8.76	2.46	3 160	LOQ (!)	2.5 (+)	9.02	13.6
Zinc plating process	83	2.38	1.48	1.95	2 189	LOQ (!)	LOQ (!)	2.5 (+)	2.5 (+)
Pre-treatment	42	2.26	1.65	1.3	4 207	LOQ (!)	2.5 (+)	4.5 (+)	5.5
Not galvanic	147	3.9	6.35	1.75	4 154	LOQ (!)	2.5 (+)	8.18 (+)	13.7

Table 17: Work-area-group - Surface treatment and electroplating –differentiated into work processes (personal and static)

Work area		Number of samples	Arithm. Mean	Arithm. Std. Dev..	Geom. Mean	Geom. Std. Dev.	50th-perc.	75th-perc.	90th-perc.	95th-perc.
			(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)
Manual assembly	static	22	3.06	2.88	2.13	3 324	LOQ (!)	LOQ (!)	4.66 (+)	5.2
Plating, generally	static	77	6.02	23.2	1.18	5 844	LOQ (!)	2.5 (+)	5.95	10.5
	personal	70	5.34	9.44	3.43	2 062	LOQ (!)	LOQ (!)	9 (+)	18.5
Plating, decorative	personal	18	3.22	4.23	2.41	1 884	LOQ (!)	LOQ (!)	LOQ (!)	4.25 (+)
	static	13	4.35	5.62	2.77	2 417	LOQ (!)	LOQ (!)	8.93	14.5
Plating, decorative, sulphuric bath	personal	13	2.59	1.04	2.45	1 400	LOQ (!)	LOQ (!)	LOQ (!)	3.65 (+)
	static	32	6.07	19.3	1.58	4 924	LOQ (!)	2.5 (+)	5.2	13.2
Hard chrome plating	personal	33	35.8	81.7	8.65	4 505	6.35	14.5	74.4	225
	static	27	57.6	188	6.74	5 307	2.5 (+)	9.58	54.6	270
Hard chrome plating, mixed acid bath	personal	16	13.8	26.8	5.97	3 135	4 (+)	11	21.8	47.6
	static	27	9.92	14	3.34	6 656	2.5 (+)	11.5	26.6	28
Hard chrome plating, sulphuric bath	personal	90	15.1	20.7	7.4	3 181	6.3	16	45	64
	static	152	10.9	22.5	3.69	4 545	2.6 (+)	8.4	29.8	40.8
Plating, black	static	15	2.84	2.21	2.15	2 389	LOQ (!)	2.5 (+)	5.25	8
Chromium plating, generally	personal	30	3.65	4.91	2.88	1 650	LOQ (!)	LOQ (!)	4.7 (+)	6.55
	static	128	3.67	10.6	1.29	4 600	LOQ (!)	2.5 (+)	5.06 (+)	7
To chromize	personal	18	3.19	2.52	2.81	1 522	LOQ (!)	LOQ (!)	4 (+)	5.8
	static	54	6.05	23.1	1.83	4 013	LOQ (!)	2.5 (+)	3.88 (+)	11.5
Laser beam surface treatment	static	12	5.5	13.4	1.24	6 072	LOQ (!)	2.5 (+)	2.5 (+)	20.7
Surface treatment, generally	personal	14	10.3	7.98	7.29	2 498	8.6 (+)	14.5	18.6	21.7

Work area		Number of samples	Arithm. Mean (µg/m^3)	Arithm. Std. Dev.. (µg/m^3)	Geom. Mean (µg/m^3)	Geom. Std. Dev. (µg/m^3)	50th-perc. (µg/m^3)	75th-perc. (µg/m^3)	90th-perc. (µg/m^3)	95th-perc. (µg/m^3)
	static	30	3.1	5.51	0.946	5 725	1.1 (+)	2.5 (+)	8	11.5
Surface coating, galvanic processes	personal	78	4.65	6.82	3.23	1 970	LOQ (!)	LOQ (!)	9.28	14
	static	110	4.57	9.95	2.03	3 906	LOQ (!)	2.5 (+)	8.5	13
Zinc plating process	personal	35	2.93	1.85	2.71	1 378	LOQ (!)	LOQ (!)	LOQ (!)	5 (+)
	static	48	1.99	0.983	1.54	2 526	LOQ (!)	2.5 (+)	2.5 (+)	2.5 (+)
Pre-treatment	personal	11	3.11	1.47	2.9	1 428	LOQ (!)	LOQ (!)	4.75 (+)	5.85
	static	31	1.95	1.62	0.978	4 797	LOQ (!)	2.5 (+)	2.5 (+)	5.5
Not galvanic	static	94	3.05	5.94	1.16	4 662	2 (!)	2.5 (+)	6	10
	personal	53	5.4	6.8	3.58	2 215	LOQ (!)	5 (+)	13.7	18.4

Table 18: Work-area-group - Surface treatment and electroplating - –differentiated into work processes (with LEV)

Work area	Number of samples	Arithm. Mean	Arithm. Std. Dev.	Geom. Mean	Geom. Std. Dev.	50th-perc.	75th-perc.	90th-perc.	95th-perc.
		(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)
Manual assembly	20	2.32	0.972	1.81	3 162	LOQ (!)	LOQ (!)	LOQ (!)	2.5 (+)
Plating, generally	104	5.32	18.9	1.53	4 982	LOQ (!)	2.5 (+)	7.9	12.4
Plating, decorative	21	2.55	2.1	2.11	1 798	LOQ (!)	LOQ (!)	LOQ (!)	4.02 (+)
Plating, decorative, sulphuric bath	40	5.62	17.2	2.35	2 936	LOQ (!)	2.5 (+)	5.6	8.7
Hard chrome plating	55	49.1	145	8.15	4 975	4.95 (+)	14.3	81	305
Hard chrome plating, mixed acid bath	40	12	20.1	4.31	5 592	5 (+)	13	28	32
Hard chrome plating, sulphuric bath	226	13.2	22.5	5.11	4 176	4 (+)	13	36.4	59
Plating, black	12	3.13	2.14	2.42	2 472	LOQ (!)	2.5 (+)	6.02	7.34
Chromium plating, generally	122	4.03	11	1.56	4 177	LOQ (!)	2.5 (+)	5.08 (+)	6.99
Laser beam surface treatment	13	5.62	12.8	1.9	4 669	LOQ (!)	LOQ (!)	2.5 (+)	18.4
To chromize	38	7.57	27.4	2.18	3 950	LOQ (!)	LOQ (!)	5.4	14.1
Surface treatment, generally	36	6.33	7.59	2.64	4 628	25 (+)	10 (+)	16.2	20.6
Surface coating, galvanic processes	150	5.11	9.71	2.68	3 073	LOQ (!)	2.5 (+)	10	17.5
Zinc plating process	47	2.36	1.88	1.8	2 328	LOQ (!)	2.5 (+)	2.5 (+)	4.13 (+)
Pre-Treatment	26	2.23	1.69	1.19	4 749	LOQ (!)	LOQ (!)	3.7 (+)	5.5
Not galvanic	101	5.01	7.37	2.54	3 512	2.5 (+)	2.5 (+)	12.8	17.9

Table 19: Work area group - Surface treatment and electroplating - –differentiated into work processes (without LEV)

Groups	Number of sam-ples	Arithm. Mean	Arithm. Std. Dev..	Geom. Mean	Geom. Std. Dev.	50th-perc.	75th-perc.	90th-perc.	95th-perc.
		(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)	(µg/m³)
Plating, generally	27	7.89	19.3	3.49	2 561	LOQ (!)	LOQ (!)	12.2	24.2
Chromium plating, generally	31	2.39	2.29	1.3	3 959	LOQ (!)	2.5 (+)	4.39 (+)	7.45
To chromize	29	2.76	3.81	1.74	3 092	LOQ (!)	LOQ (!)	2.85 (+)	3.68 (+)
Surface coating, galvanic processes	26	2.74	2.04	1.82	3 498	LOQ (!)	LOQ (!)	4.3 (+)	7.21
Zinc plating process	32	2.41	0.729	2.13	2 082	LOQ (!)	LOQ (!)	LOQ (!)	LOQ (!)
Pre-treatment	13	2.42	1.74	1.49	3 893	LOQ (!)	2.5 (+)	4.25 (+)	5.45
No galvanic	44	1.4	1.07	0.729	4 260	LOQ (!)	2.5 (+)	2.5 (+)	2.5 (+)

Within the evaluation tables the following abbreviations and indexes are used:

LOQ	Limit of quantification
(!)	The specification of a cumulative frequency concentration in the results table is not made, as there are more measurement values below the analytical limit of quantification (LOQ) , as measurement values are represented by this cumulative frequency value
(+)	Distribution value is below the largest limit of quantification (LOQ) of the data collective.
Arithm. Mean	Arithmetic Mean
Arithm. Std. Dev.	Arithmetic Standard Deviation
Geom. Mean	Geometric Mean
Geom. Std. Dev.	Geometric Standard Deviation
Perc.	Percentile

Technical measures are usually implemented in cases where the specific workplace situation leads to higher emissions of gas, vapour mist or dust. This can be the case for example, if large quantities of the substance are handled in an open environment or if it is processed e.g. at high temperature. In contrast, emissions of the same substance are comparatively low if it is used e.g. in small quantities or if it is processed at room temperature.

This means summarized:

The result of using technical measures is usually that the exposure level in workplaces with high emissions is brought roughly into line with the workplaces with low emissions and no technical measures. Hence the apparent paradox of workplace with local exhaust ventilation having often the same or even higher exposure levels than those without local exhaust ventilation.

The presented data are suitable to demonstrate that there is a large cohort of exposed workers representing a widespread use.

The European Union Risk Assessment Report on Chromium trioxide (and other chromates, Vol 531) draws the conclusion, that there is a need for limiting the risks and that risk reduction measures which are already being applied shall be taken into account.

Based on the more recent exposure information from the MEGA database presented above and taking account of the additional information in the RAR [EC, 2005] the following industry sectors worker exposures are found for which further risk reduction measures are judged to be needed:

- Formulation of metal treatment products
- Use in electrolytic metal treatment
- Decorative plating and hard chrome plating
- Use as a fixing agent in wood treatment

CONSUMER EXPOSURE

The Swedish product register has evaluated the exposure potential of chromium trioxide and chromic acid in registered preparations for human consumers. According to this evaluation, a potential exposure of human consumers may derive from use of “other laboratory chemicals” with a chromium trioxide concentration between 0.1 % and 1.0 % in human health and social work activities. A probable exposure of human consumers may derive from use of water based paint with anti-corrosive effect and a chromium trioxide concentration between 1 % and 10 % for maintenance and repair of motor vehicles [KEMI, 2010].

The Risk Assessment Report [EC, 2005] describes two scenarios for consumer exposure to copper chrome arsenate (CCA) treated wood. According to this assessment, construction of a fence by an adult person results in an internal exposure from wood dust inhalation during wood cutting of 0.029 µg Cr^{VI}/kg body weight and in an internal exposure of 1.6 µg Cr^{VI}/kg body weight from dermal contact to wood dust. A five year old child playing on wooden equipment would be internally exposed to 0.08 µg Cr^{VI}/kg body weight by dermal contact of hands and to 0.1 µg Cr^{VI}/kg body weight by the oral route (hand to mouth contact). This assessment is limited to CCA treated wood, and it may not represent the current situation, as CCA formulations have been restricted by Commission Directive 2003/2/EC. Moreover, there is no information on Cr^{VI} residues in treated wood imported into the European Union. Therefore, recent data on Cr^{VI} contents in the remaining biocidal products on the European market, on Cr^{VI} residues in treated wood and on their leachability into body fluids are needed to assess consumer exposure from chromic acid (chromium trioxide) as a fixative in wood preservatives.

ENVIRONMENTAL EXPOSURE

The following information on environmental exposure was taken from the Risk Assessment Report on chromium compounds, published by the ECB in 2005 [EC, 2005].

Main uses of chromium trioxide are metal finishing and manufacture of wood preservation products. During the use of Chrome trioxide, the Cr^{VI} is mainly converted into other oxidation states. Concerning metal finishing Cr^{VI} is converted into metallic chrome. Concerning wood preservation Cr^{VI} is reduced to Cr^{III}. Wastewater containing relevant amounts of Cr^{VI} is usually treated according to local legislative allowances before discharge to sewer and/or a biological wastewater treatment plant. The most common methods for lowering the concentration in wastewater involve reduction of Cr^{VI} to Cr^{III} using ferrous sulphate, sodium bisulphite, sodium metabisulphite or sulphur dioxide at low pH, followed by raising the pH to around 9.5, to precipitate the insoluble chromic hydroxide formed. Due to the low volatility of Cr^{VI} emissions to air are unlikely. Sludge application is another potential route to the terrestrial compartment; however, from comments from producers and users it is more usual for solid waste and sludges to be disposed of to landfill or to be sent to dedicated facilities for recycling. Hence an exposure to the environment is expected to be limited.

Geochemical factors play an important role in speciation and fate of chrome. Releases of Cr^{VI} from any sources are expected to be reduced to Cr^{III} in most situations in the environment. Cr^{VI} can be reduced to Cr^{III} under anaerobic conditions found in the environment by both biotic and abiotic processes, including reaction with Fe^{II}, sulphides, organic matter and anaerobic micro-organisms. Oxidation of Cr^{III} to Cr^{VI} can occur, but the process is only likely to be significant in aerobic soils and sediments where high concentrations of manganese dioxide (the only known environmental oxidant for Cr^{III} exist. Under these conditions, a 2-3% of the Cr^{III} present may oxidise to Cr^{VI}. Again, any Cr^{VI} formed in the soil or sediment may be subsequently transported to anaerobic layers where rapid reduction back to Cr^{III} could occur. The impact of Cr^{VI} as such is therefore likely to be limited.

3 CURRENT KNOWLEDGE ON ALTERNATIVES

3.1.1 (Metal) surface treatment or metal finishing[6]

Research in the replacement of hexavalent chrome from conversion coating started over 15 years ago, before environmental regulations were enacted [Prosurf, 2008a]. Directive 2000/53/EC on End-of-Life Vehicles (ELV Directive) [EC, 2000] and Directive 2002/95/EC on the Restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS) [EC, 2002] were the most drivers for R&D activities for replacement of chromium-VI compounds in metal surface treatment. By now the automotive industry has introduced Cr^{VI}-free coating systems in most of the connecting elements [Rybka, 2008]. Currently, there are about 30 different alternatives for chromium (VI) coating systems available on the market [Mairhöfer, 2008]. There is no drop-in solution in replacement of chromium-VI based surface treatment technologies; however individual solutions could be found for different applications and market segment. The most feasible alternatives, which could be found by literature and internet research, are described below.

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[6] In this section several alternatives were described which could be feasible from the technical point of view for replacement of Cr^{VI}-compounds in metal finishing. The Hazardous Assessment was not done in the dossier in detail. This should be made later in authorization process. Additionally, some examples with trade name were mentioned in the section 3.1.1, but they do not cover the full market/offer on alternative products in the branch.

3.1.1.1 Thermal spray and HVOF (High Velocity Oxy Fuel)

The most commonly used technology for replacing hard chrome plating is thermal spray (primarily, but not exclusively, HVOF) [Hazmat-Alternatives, 2010a]. Thermal spray is the general term for a number of processes in which particles of coating materials are heated and sprayed using high speed gas onto the surface to be coated. It is a fully commercial industrial process that is used for coating everything from bridges and radar towers to aircraft parts and prosthetic knee joints. Further application examples for the HVOF coatings could be extracted from TURI report [TURI, 2006]:

- General Manufacturing Industry: Extrusion Dies, Thread Guides, Forging Tools, Wire Drawing Capstans, Cam Followers, Roller Bearings, Hot Forming Dies
- Gas Turbine Industry: Turbine Nozzles, Jet Engine Ducts, Jet Engine Manifold Rings, Gas Turbine Fan Seals, Aircraft Flap Tracks, Expansion Joints, Mid Span Supports (Fan Blades)
- Petroleum Industry: Pump Plungers, Liners, Sleeves, Compressor Rods
- Chemical Process Industry: Gate Valves, Pump Components
- Paper/Pulp Industry: Printing Rolls, Digesters, Liquor Tanks
- Automotive Industry: Piston Rings, Cylinder Liners

Since thermal spray coatings are readily sprayed up to 500 microns thick, they are good for rebuilding worn components, which is the primary use for hard chrome plate. There is a large choice of coating materials, starting powders, gases, types of equipment and deposition conditions. The most common coating materials for chrome replacement are chrome carbide-nickel chrome (Cr_3C_2-NiCr) and tungsten carbide-Co (WC-Co and WC-CoCr). Cr in these materials is not hexavalent. If done well, thermal spray will give a higher quality, more reliable coating with much longer service life [Hazmat-Alternatives, 2010a].

3.1.1.2 Vacuum coatings

For some applications these types of coatings can be cost-effective, especially for small components [Hazmat-Alternatives, 2010b]. Deposited coatings show long time service, high strength as well as high performance and resistance. [Bach, 2004]

There are two primary types of vacuum deposition methods:

a) Physical vapor deposition (PVD)

   In this method the coating material is created from a solid, either evaporated by an electric arc or an electron beam, or sputtered. It goes through plasma (to allow the ions to be accelerated) and lands on the component surface, forming a very thin but very hard layer.

b) Chemical vapour deposition (CVD)

   CVD processes have a lot in common with PVD, including cost and the size of items that can be coated. However, in the CVD method the coating material comes from gases that combine on the hot surface to form a coating.

The sizes of products that can be coated are less than a foot or 30 cm.

Further information and details about these coating technologies could be found on:
http://www.hazmat-alternatives.com/Alt_tech-Chrome_Alts-VC.php.

Various very hard PVD and CVD coatings have been put forward as general-use chrome alternatives, including titanium nitride (TiN), diamond-like carbon (DLC) and tungsten carbide (WC, Hardide). While these types of coatings are widely used commercially (TiN for dies, molds and drills, diamond-like and WC-C carbon for diesel fuel injector rods, PVD ZrN for “lifetime coatings” on faucets and door hardware for example). There is some usage of coatings such as TiN on aircraft components such as engine bearing races and APU (Auxiliary Power Unit) components [Legg, 2006]. Potentially they may be cost-effective for small components that exhibit abrasion wear and components that are removable and replace items rather than repair components, such as small hydraulic rods, hydraulic spool valves and pumps.

3.1.1.3 Zinc based alternatives

The desired corrosion resistance of surface coating could also be achieved by using - instead of pure zinc in the offshore layer – several zinc alloy layers (ZnFe, ZnNi oder ZnCo) [Wikipedia, 2010; Galvanotechnik, 2005]. These types of layers could be combined with other finishing treatment methods like thick or thin-film-passivation e.g. with Cr^{III} see chapter 2.1.1.5 and optionally sealing. In general it could be distinguished between zinc flake and zinc alloy plating systems. For more details see table “Technical overview of possible methods for replacement of chromium (VI)-compounds in metal surface finishing”. Currently ZnNi-layers are being used for connecting elements producing [Becker, 2008]. Currently significant market growth for Zink/Nickel coating systems can be observed, because they were improved and show also gloss/shining as well as decorative properties. Additionally a zinc/nickel-system has good resistance by high temperatures (up to 150 °C), so a long life time is made possible [Wikipedia 2010; Galvanotechnik, 2005].

The automotive industry requires Cr^{VI}-free layers with high corrosion resistance. Modern techniques consist for example of basic ZnNi, black passivation and sealer and match the high technical requirements. This type of metal finishing has mainly being used to produce bolts, screws and bolted joints. The fastener industry has partly successfully introduced the new technologies (Cr^{VI}-free electroplating and Cr^{VI}-free zinc flakes systems) to provide Cr^{VI}-free coatings, for example:

- Corrosion protection for bolted joints – e.g. the use of zinc flake Systems for wind turbines.
- Hexavalent-chrome-free zinc flake systems are commonly used in the automotive industry to provide effective corrosion protection. However, these multifunctional systems are also ideally suited due to their technical properties to use in other areas of industry. [Reusmann, 2009]

Thermal diffusion galvanizing (“TDG”) is a new "green" process which creates a zinc coating metallurgically similar to hot dip galvanizing. Instead of dipping parts in molten zinc, zinc is applied in powder form with accelerator chemicals. The parts and the zinc compound are sealed in a drum which is rotated in an oven. Due to accelerator chemicals added to the zinc powder, the zinc/iron diffusion (alloying) takes place at a lower temperature than hot dip galvanizing, and results in a more uniform and wear resistant coating. The process also eliminates the need for hazardous caustic acids and flux baths required to prepare parts for hot dip galvanizing. The unique crystal structure formed by the process provides a strong bond with paint, powder coating and rubber overmolding processes [Chemie.de, 2010], trade name: e.g. ArmorGalv® [DiSTeK, 2010].

3.1.1.4 Nickel-based alternatives

Many nickel-based coatings can be used as alternatives to hexavalent chromium finishes. Nickel with tungsten added provides hardness up to 800 VHN and up to 1,000 VHN or up to 1,200 VHN for Ni-B [Legg, 2006] after heat-treating [Graves, 2005]. Unfortunately these hardness values are only achieved by heat treating at 400°C. Other nickel-based coatings include nickel-boron, nickel-cobalt-phosphorus, nickel-phosphorus, nickel-phosphorus-tungsten and nickel-molybdenum. Electroless nickel and electroless nickel alloy coatings also have been tested as potential alternatives to hard chromium plating. The most common are nickel-boron and nickel-phosphorus. The hardness of nickel-alloy coatings depends on the composition, reducing agent concentration and type of heat-treating. Testing has shown that there is no correlation between hardness and composition with heat-treated finishes; however ductility increases when the phosphorus content is increased. Electroless nickel composite coatings infiltrated with boron nitride, diamonds, molybdenum disulfide or silicone carbide particles have hardness values between 900 and 1,200 VHN. Coating hardness depends on composition, concentration of the reducing agent, heat treatment and particulate additions. Particle size also affects hardness; larger particles result in greater hardness. For internal diameters (ID) and other low-stress areas, however, the highest hardness is not usually needed, and electroless or electroplated Ni is often used for IDs of aircraft landing gear outer cylinders and other hydraulics [Legg, 2006]. Maintenance of electroless plating bath chemistry is much more critical than hard chrome baths, since electroless baths must maintain a delicate balance to keep the metal salts in solution, yet autocatalytically depositing on substrates placed in the bath. A variety of electroless Ni composites are available commercially. Some contain hard particles such as diamond or SiC for wear and/or PTFE for lubricity. For example, NiPlate 700, which AFRL (Air Force Research Laboratory) has identified as the best ID chrome alternative, contains SiC particles. There are several commercial and near-commercial electro- and electroless plates.

3.1.1.5 Chromium (III) based coatings

It is reported that Cr^{III} based conversion coatings are increasingly being used in the practice as alternative for Cr^{VI} conversion coatings (passivation) [Galvanotechnik, 2005]. Additional corrosion/wear protection level could be achieved by using the second barrier layer – sealer or Topcoats. For example on Cr^{III} based SurTec 650 chromitAL® layer is an Cr^{VI} -free alternative for yellow chromating on aluminium and alloys, it shows similar technical features (corrosion protection, primer for coatings, contact resistance) [Volk, 2006]. The passivation with Cr^{III} on zinc and zinc alloys has been successfully applied since long time [Volk, 2006]. Further application examples [Schweizer, 2009] are corrosion protection on alumina, pre-treatment for powder coating or liquid painting, pre-treatment for bonding and treatment after Anodising [Galvanotechnik, 2005]. Typical Cr^{III} passivates contain now Co or silica nanoparticles to enhance the thin Cr^{III} films. Rather than Cr^{VI} precipitating into any scratch in the coating, the SiO_2 nanoparticles fill the exposed area to prevent further corrosion. As a result of these improvements, e.g. 4th generation TASDIP-175® passivate products show that Cr^{III} on Zn coating is practically the same as Cr^{VI} [Legg, 2007]. Additionally Cr^{III} coatings are widely used for decorative chrome plating [Legg, 2006]. In conclusion it can be said that replacement of Cr^{VI} -layers by Cr^{III} -systems is in many cases possible and these coating systems are widely used in different industries [Galvanotechnik, 2005]. Recently the use of Cr^{III} electrolytes to perform hard chrome plating was achieved by R&D activities. For more information see table “Technical overview of possible methods for replacement of chromium (VI)-compounds in metal surface finishing” and http://www.ipa.fraunhofer.de/index.php?id=173.

3.1.1.6 Part modification

A further possible alternative is to re-engineer or redesign the part or use different substrates, such as improved wear and/or corrosion resistant steels designed for specific applications [Graves, 2005]. Surface modification can also be applied. Heat can diffuse elements into the near surface region of a substrate to form an alloy or compound layer with improved properties, such as hardness or lubricity. The names of some of the processes are derived from the type of element used: nitriding (nitrogen), boronizing (boron), and carburizing (carbon) plasma diffusion is the process whereby elements are introduced into the surface of the substrate by the use of a gas activated with the desired element at elevated temperatures. Variations on this process include plasma nitriding, nitrocarburizing, and low pressure nitiriding [TURI, 2006]. Plasma surface ion implantation of coatings is also used commercially. Other surface modification techniques include laser alloying, whereby a precursor mixture is applied to the part. This mixture is then heated to fuse the coating. Another type of surface modification is electrolytic diffusion, which includes plasma/arc processing [Graves, 2005]. Nitriding and carburizing are widely used industrially (in fact most gears in military equipment are carburized, as they are in most commercial equipment). However, they are only suitable for Original Equipment Manufacturing (OEM) use. Nitride treatments are used for some components, such as gun barrels [Legg, 2006]. In general heat treatments are used to make surfaces more resistant to wear, corrosion or oxidation [TURI, 2006]. As a replacement for hard chrome, it may be used in combination with another process. For example, a substrate is hardened with plasma nitriding, and then coated with a Physical Vapour Deposition (PVD) process. For example TENIFER®-QPQ- is a modern heat treatment technology, it is applied to coat the components (e.g. transmission shafts, hydraulic power unit, piston rods, by utility vehicles: crank shafts, steering wheels etc. [Boßlet, 2009]) of steel, cast iron and sintered iron materials, which are used in different industries to provide wear and corrosion resistance like by hard chrome plating [Boßlet, 2004].

3.1.1.7 Further possible alternatives

In addition there are several possible alternative methods for Cr^{VI} replacement available on the market. Nanocrystalline coatings consist of diverse alloys, but Co-P and Co-P/diamond coatings meet or exceed the hard chrome standard [TURI, 2006]. Hybrid polymer coating materials (ORMOCER®s) are an innovative solution for the surface treatment and functionalization of metals, plastics, glass and natural products and they can be used for surface protection against mechanical wear and corrosion [Fraunhofer ISC, 2010]. Furthermore sol-gel nano coating-systems consist also of organo-metallic composites. This type of coating provides high corrosion resistance and hardness as well as temperature resistance and other technical properties [Heiche Oberflächentechnik, 2009]. Sol-gel coatings provide excellent paint adhesion and can be formulated for different substrate and primer chemistries [Legg, 2007]. Sol-gel coatings are used on diverse basic materials for example in automotive industry [Heiche Oberflächentechnik, 2009]. Other alternative substances and technologies (available at present time and in development/trial stage) are described in the Road Map for Surface Finishing industry (Part 1, PROSURF European project no. 023270) [Prosurf, 2007; Prosurf, 2008b].

3.1.1.8 Conclusion on alternative methods for chrome metal finishing/surface treatment

In conclusion it can be said, that the described above alternative layers (systems) are partly established for industrial use or some of them are now in development/trial stage. Several layers provide good quality just in combination with each other and optionally coats/ sealers are needed. Thus, the trend goes to use of complex layer systems/multilayer systems.

Furthermore technology trends were evaluated in the report “The Future of Finishing”. These are [Chalmer, 2008]:

- **Change to “greener” process chemistries –**Change to alternative “green” chemistries that can meet surface finishing process requirements while reducing or eliminating the use and generation of hazardous substances.
- **Change from “wet” processes to “dry” processes** – Change from conventional surface finishing immersion chemistry solutions to alternative metal deposition technologies (e.g. HVOF or PVD)
- **Change substrate materials from finished metals to non-metals** – Change materials and manufacturing processes from metal finishing to non-metals, such as composites or plastics
- **Develop new metal alloys that reduce surface finishing requirements** – Use new metal alloys that provide sufficient corrosion resistance and reduce or eliminate the need for metal

finishing using toxic chemical processes (e.g. new stainless steel alloy that can replace steel coated with cadmium)

- **Develop processes based on nanotechnology** – Use nanocrystalline metal coating processes or using nanomaterial-enhanced metal or non-metal substrates.

Table 20: Technical application of possible alternatives for chromium (VI)-compounds in metal surface finishing

Alternatives to Chromium-VI-compounds in metal surface finishing		Chemical substances used for surface treatment	Readiness for marketing / Commercial use	Additional information, examples of application
I. Trivalent Chromium	**Conversion coating:**	• involves the use of several chemical mixtures, which vary according manufacturer • Chrom(III)-nitrat-Nonahydrat (concentration of 40-60 %) • not all but some processes may also contain Cobalt-(II)-nitrat-6-hydrat (concentration of 1-3 % or 3-7 %) or silica nanoparticles	• feasible for a range of generic markets, current available on the market • based on Cr(III) thick-film passivation on zinc and zinc alloys have been using for some time current R&D activities on Co-free passivation	• conversion coating (substrate: steel, aluminium) • (yellow) chromating alternative (substrate: zinc, zinc alloys and aluminium, magnesium) • connecting elements, automotive industry • anti corrosion use, e.g. in OEM branch (ABS-cap, torque support, shell part etc. • good electrical properties.)
	Decorative plating	• chromium(III) chloride electrolyte	current available on the market	• substrate: plastics, steel, aluminium • sanitary, furniture industry, architecture, fitting industry e.g. window frames etc.
	Hard chrome plating:	• Chromium(III) compound (most appropriate ammoniumchromalaun) buffer: aluminum sulphate (most appropriate) + complex binder: glycine	• construction of pilot plant in industry-standard (now in trial stage) Best-case scenario available in 3 years on the market and then after 5 years max. 10% of the hard chrome plating market could be replaced by Cr(III)-technology	• electrolytic deposition of technical chrome layers (with any film thickness) • application in several industries could be possible with restriction: applicable only for rotation-symmetric parts and not 3D-parts, cause of geometry issue
II.	**Nickel based**	a) nickel plating • some plates based on other alloy coatings: Ni-W, Ni-W-B, Ni-P and Ni-W-B with SiC b) Nickel-silicium carbide with hard Matrix electrolytic deposition of Nickel-silicium carbide layers c) Electroless diposition of Ni or Nickel-silicium carbide) d) Nickel composite layer strengthened with titanium dioxide nanoparticles	a) commercially available b) commercially available c) widely available plating process, commercially available d) no data available yet	a) substrate: all metals. • For decorative uses as well as for corrosion protection purposes. • Application due to hard layers in Electrical Apparatus and Telephone industry. b) alternative for hard chrome plating • high temperature resistance • high abrasion - and corrosion resistance • Ni-SiC-layers as coating for cylinder

Alternatives to Chromium-VI-compounds in metal surface finishing	Chemical substances used for surface treatment	Readiness for marketing / Commercial use	Additional information, examples of application
			liners in the automotive industry, e.g. in formula-1-engines as well as established in series manufacturing • internal coating of pipes, e.g. scraped-surface exchangers in the food industry c) Electroless Ni is most useful for small components. The coating is very corrosion resistant as-deposited, provided there are no holes or scratches, but loses some corrosion resistance on heat treating are often used for mirrors and very smooth dies and molds. d) no data available yet
III. Zink-based	1. Zinc flake systems: the coat consists of zinc and aluminium and other elements lamella mix a) Zinc-flake systems, silver-coloured b) Zinc-flake systems, black-coloured	Feasible for a range of generic markets 1**.** Zinc-flake systems: a) silver coloured • several years series production experience Delta Tone© + Delta Seal©, systems are in very widespread use for series production • new system Delta Protekt KL 100© in series operation with several coating subcontractors and one in-house operation, mostly in combination with topcoat Delta Seal GZ©,Delta Protekt VH 301© undergoing trials / being introduced • the systems Delta Protekt KL 100© + Delta Protekt VH 301© at trials stage • the new systems Geomet© + topcoat (e.g. PLUS L©) in series operation at two coating subcontractors • systems of other suppliers (Magni, Kunz) are now available on the market b) black coloured	1. Zinc-flake systems: • The main focus on screw threads/ wires, the main application in the automotive industry. Zinc-lamella systems have good corrosion protection ability. Recently have been wide used in other application fields for examples aerospace industry • Application examples: springs, spring-loaded band-type clamps and clips, brake discs and brake drums. • MKS (Micro-layer corrosion protection system) -Systems (Delta-Tone and Delta-Seal) have been used successfully in wind turbines for 15 years

Alternatives to Chromium-VI-compounds in metal surface finishing	Chemical substances used for surface treatment	Readiness for marketing / Commercial use	Additional information, examples of application
	2. Zinc alloy plating systems a) Zn + “thin-film” passivation + transparent sealer b) Zn + “thick-film” passivation (+transparent sealer) c) ZnFe; phosphate-coated +black-pigmented sealer black d) ZnNi + thick-film passivation (+ transparent sealer) e) ZnNi + black passivation (+ transparent sealer)	• Delta Tone$^{\copyright}$ / Delta Protekt KL 100 + Delta Seal GZ sw$^{\copyright}$ systems are now in series production • Recently, some manufacturer have introduced further systems with black topcoats, several of them are already in serial production 2. galvanic systems a) several process lines in series operation, currently the most applied Zn-system b several process lines in operation since1998 c) in use for several years in one plant d) since 2002 several process lines in series operation e) a few lines in series operation since 2002	2. Zinc-Nickel alloy plating systems fulfill extreme high corrosion protection requirements in the automotive industry a) barrel and rack b) barrel and rack c) coil-coating application in the automotive industry, decorative use with good corrosion resistance (barrel) d) mainly in the automotive industry: parts in motor, steel bands e) Zinc-nickel-layer + passivation + sealing (inorganic material):e.g. for hydraulic joining elements, surface protection layers for hydraulic-precision steel tubes (especially mobile hydraulic)
IV. **Dry plating Alternatives** a) CVD-Hard Coating b) PVD	• applicable on all materials as substrate a) Microfabrication processes widely use to deposit materials in various forms, including: monocrystalline, polycrystalline, amorphous, and epitaxial. These materials include: silicon, carbon fiber, carbon nanofibers, filaments, carbon nanotubes, SiO_2, silicon-germanium, tungsten, silicon carbide, silicon nitride, silicon oxynitride, titanium nitride, TiCN (Titancarbonitride) b) TiN, TiCN, TiAlN, Cr(III)N, CrAlN, ZrN, SiC, DLC, MoS_2	• CVD/PVD-techniques are now industrial established • feasible for a range/(niche) of generic markets	• Hard chrome plating alternatives • Substrate: steel systems a) The process is often used in the semiconductor industry to produce thin films b) Deposit of chromium nitrure as a replacement of the hard chromium plating. Tool kits and building elements, coatings on implant for medical use; coating on plastics is the greatest market (e.g. wheels, damper, headlamps etc. in the car) • TiN for dies, molds and drills, diamondlike and WC-C carbon for diesel fuel injector rods, PVD ZrN for “lifetime coatings” on faucets and door hardware for example.

Alternatives to Chromium-VI-compounds in metal surface finishing	Chemical substances used for surface treatment	Readiness for marketing / Commercial use	Additional information, examples of application
V. Thermal Spray Technology a) HVOF carbides b) HVOF alloys c) HVOF NiAl d) Cold (kinetic) spray materials e) Plasma-arc spraying carbides and alloys f) Electric-arc spraying g) Flame spray	a) chrome carbide-nickel chrome (Cr_3C_2-NiCr) tungsten carbide-Co (WC-Co and WC-CoCr) b) (e.g. Tribaloys, stainless steels) c) NiAl d) Alloy powder e) Powder (tungsten and chrome carbide, Ni alloys, oxides) f) The molten wire is the feedstock material for creating a coating, e.g. Zn and ZnAl g) combustion of gases melt powder, wire or rod material and propel the molten droplets onto a surface to create a coating	**Usage:** a) Industrial hydraulics, rolls, airframes and engines b) Hydraulic IDs, bearing journals, airframes and engines c) Worn components d) Carbide sprays not commercially proven. Still in development. e) Wear coatings, thermal barriers Worn components, journals, etc, turbine engine components, hydroelectric turbines f) corrosion protection of bridges, communications towers, concrete g) coatings out of a wide range of materials from plastics to oxide ceramics	a) Primary wear coating alternative to chrome plate b) Less wear resistant than carbides, but less brittle and more machinable c) Relatively soft, used for thick build-up. HVOF equivalent to sulfamate Ni d) Most only capable of spraying soft materials and alloys. e) the most versatile of the all the thermal spray processes capable of spraying all materials; Major use in engines is thermal barriers, not Cr replacement f) Zn and ZnAl for corrosion coating of metal structures such as communication towers and bridges g) Repair of some components, e.g. Zn and Al coatings for corrosion.
VI. Partmodification Heat treatment process a) Plasma treatment diffusion b) Nitrocarburizing c) DLC (diamond like carbon)	• Substrate: ferrous, steel a) e.g. PPD™ - Surface Composition: • Diffusion Depth: Finely dispersed precipitations (developed primarily from N and C elements) • Examples of treatable base materials: - Cold and hot work steels - Nitriding and plastic moulding steels - Quenched and tempered steels b) Salt bath nitrocarburizing (alkali cyanate and alkali carbonate) c) The optimum multilayer structure series is: titanium, titanium nitride, titanium carbonitride, titanium carbide, and then the DLC. Several methods have been developed for producing diamond-like carbon films: • primary ion beam deposition of carbon ions (IBD)	• feasible for a range/niche of generic markets, short-term (2008-2010) available b) Salt bath nitrocarburizing by the TENIFER®-process has been applied in a wide range of industries throughout the world for many decades.	a) alternative for hard chromating • (e.g. thermal barrier coatings and abradables in gas turbines) • e.g. PPD™ Technology: application for large (press) tools b) alternative for hard chromating TENIFER® /QPQ®-PROCESS • used to improve the wear resistance, the fatigue strength and – in particular when combined with the oxidative cooling – the corrosion resistance of components made from steel, cast iron and sintered iron materials. • used for components in the aircraft, motorcycle and utility vehicle industry, in offshore technology, in the construction of plant and machinery, in energy technology, in the food industry as well as in

Alternatives to Chromium-VI-compounds in metal surface finishing	Chemical substances used for surface treatment	Readiness for marketing / Commercial use	Additional information, examples of application
	• sputter deposition of carbon with or without bombardment by an intense flux of ions (physical vapour deposition or PVD) • deposition from an RF plasma, sustained in hydrocarbon gases, onto substrates negatively biased (plasma assisted chemical vapour deposition or PACVD)		the manufacture of textile machines, hydraulic aggregates and optical equipment. c) A wide variety of objects are now being coated, ranging from small items, to large dies and moulds. The rapidly expanding uses of the DLC films developed by the hybrid technique includes: • decorative/low friction coatings • coating of tools for the high speed machining of aluminium and copper alloys • ceramic washers in mixer taps • guides in textile processing machines • punches/dies • seals • cutting taps
VII. Nanocrystalline Coatings	a) Hybrid Polymer Coating Materials (silicone, organic polymers, glass/ceramic Al_2O_3, TiO_2; ZrO_2) => ORMOCER® Other sol-gel coating-systems • Nanocomposite 1, Silan-Al • Nanocomposite 2, Silan-Al-Polymer • Nanocomposite 3, Silan-Al/Zr • Nanocomposite 4, Silan-Al/Zr-Polymer b) alloy coatings: • cobalt-phosphorus (Co-P) • Co-P metal matrix combined with the hard particulates (such as Cr_3C_2 or SiC) dispersed throughout • Co-P/diamond coatings	a) no information available yet b) just now becoming commercially available	a) very good corrosion protection for several industrial uses Substrate: aluminum, magnesium, steel, zinc, copper etc Application examples: no data available b) The coating can be applied through electrodeposition, vapor deposition, or spray conversion processing application in automotive and aeronautic, e.g. Hard TriCom (It consists of a cobaltphosphorous metal alloy matrix with hard particulates uniformly dispersed within it). Engineering: thickness can be achieved for both original equipment manufacturing (OEM) or overhaul and repair (O&R).
VIII. Vacuum Deposition technology	Alloys of unknown nature (but alloys contain no Cr^{III}, Cr^{VI}, Ni, Cu)	The Chrom-Optics® process has successfully passed numerous tests by the automotive industry, the furniture industry and even the sanitary industry.	The Chrom-Optics® process is based on new findings about chemical reactions which enable a new type of coating system. • a corrosion resistant composite is produced

Alternatives to Chromium-VI-compounds in metal surface finishing	Chemical substances used for surface treatment	Readiness for marketing / Commercial use	Additional information, examples of application
(no CVD/ PVD) Chrom-Optics®		Trial stage was successfully completed. Started with series production in 2008	in the gloss layer. • it is visually indistinguishable from electro-deposited chromium. • among other things, it can be applied to metal and plastic parts. Automotive: Wheel rims Exterior (reflectors / bumpers / strips / exhaust systems / mirror holders / roof rails / holders for parking aid sensors) Interieur (Embleme Interior (emblems / strips / decorative rings / rear load sills / control panels, etc.) Two-wheel industry Other industries The whole hardware industry The whole fittings industry (sanitary and others) The whole communication sector The whole profiles/beadings sector Accessories Lifts, escalators/travellators/pavements Complete furniture and interiors sector: frames, bases, counters, displays Complete architecture Decorative bathroom and other radiators
IX. Hard anodizing	anodic oxidation on aluminium alloys	Currently available on the market	• especially hard and wear resistant oxid-layers typically application examples: piston, cylinder, cylinder liners, shock absorber for automotive, hydraulic devices, parts for gas turbine, office machine, tools, food processing and transmission

Alternatives to Chromium-VI-compounds in metal surface finishing	Chemical substances used for surface treatment	Readiness for marketing / Commercial use	Additional information, examples of application
X. Anodising	anodic oxidation of Aluminium	Currently available on the market	• excellent corrosion resistance • improved abrasive and wear resistance due to high hardness • **Electrical engineering**: Conductor rails, motor winding, non-magnetic circuits, parts for generator • **Automotive:** bodies, Rims, Engine blocks, Pistons, Brake Cylinder, Connecting rods etc. • **Engineering:** office machines, optical devices, Bicycle frames, printing press and folding machines • **Aerospace industry:** Fuel Lines, Fuselage frames, lining • **Chemical Industry:** Pipelines, mixers and stirrer, container
XI. Others a) NiCom® b) TriCom®	a) NiCom Nickel Silicon Carbide Dispersion Coating b) Coating: cobalt metal matrix combined with chromium carbide Cr_3C_2 particulates uniformly dispersed within it.	Available on the (U.S.) market	a) Typical Applications: Internal combustion engines, aircraft, marine, and oil industry components. b) Typical Applications: Aircraft seals, ducting, etc.

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Personal communication with innovators of alternatives

3.1.2 Specific application in wood preservation

Cr^{VI}-containing mixtures are used as fixing agents for wood preservations. In that context it is mostly used in water-borne chromated-copper preservatives. Especially the use of copper-chrome-arsenic (CCA) mixtures was common for many decades. Through the last years a number of regulatory authorities established restrictions for CCA which increased the number of copper-based wood preservatives without the requirement of Cr^{VI}. Indeed Cr^{VI} seems to have little or no direct biocidal activity but rather serves as stabiliser of preservative components like copper [Freeman, 2008].

A possible Cr^{VI}-free alternative for wood preservation is Copper-HDO which is already used in Europe and under approval in the United States and Canada [ACE Blasting & Finishing, 2009]. Besides alkaline copper quaternary ammonium compound (ACQ) and copper azoles have already come into wide use in the USA, Europe, Japan and Australia. Further copper based preservatives are copper naphthenate and oxine copper. Quaternary ammonia salts (e.g. benzalkonium chloride) and triazoles (e.g. propiconazole and tebuconazole) can not only be used as co-biocides augmenting copper preservation but also serve as preservatives on their own [TRGS 618, 1997]. Besides cyroconazole, propiconazole polymeric betaine can substitute Cr-containing mixtures.

Copper remains the primary biocide component used to protect wood used in ground contact or fully exposed to the weather since it shows good biocidal activity [Lebow; 2004]. Recently the micronized or dispersed copper preservation technique has been introduced to the USA and Europe. The nano particles are dispersed in water and depending on their size penetrate the wood cell walls. The performance in preservation is comparable or better than in soluble copper based counterparts [Freeman, 2008].

Another new technology is the wood acetylation in which free hydroxyl groups responsible for high susceptibility of wood to climatic conditions are transformed to acetyl groups. Acetylated wood is non-toxic and does not bear the problem of leaching compounds affecting the surrounding environment [Rowell, 2008].

For further information see the website of the US EPA[7] about alternatives for Chromated Copper Arsenate (CCA) or the website of USDA Forest Service wood preservative alternatives.

4 RISK-RELATED INFORMATION

Chromium trioxide shows various toxicological properties like acute and chronic toxicity, corrosivity as well as skin and respiratory sensitisation. Furthermore chromium trioxide is a reproductive toxicant, a germ cell toxicant and in particular, a carcinogenic substance. The carcinogenic property via inhalation, which is induced by hexavalent chromium, seems to be the most prominent toxicological endpoint for a quantitative risk assessment. Therefore, this dossier is focussed on carcinogenic properties of chromium trioxide solely.

Quantitative risk estimates for occupational long-term exposure of hexavalent chromium were published by several authors and authorities. These estimates are based on human data derived from occupational settings.

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[7] www.epa.gov/oppad001/reregistration/cca/index.htm#alternatives

The Risk Assessment Report on chromium trioxide, sodium dichromate, sodium chromate, ammonium dichromate and potassium dichromate [EC, 2005; annex H] includes a quantitative risk assessment for Cr^{VI} compounds which is based on studies of Mancuso [1975, 1997] and evaluations from US EPA [1998a, 1998b]. Assuming Cr^{VI} to be a non-threshold carcinogen risks were calculated by linear extrapolation. Occupational exposure levels of 50 µg/m^3 and 1 µg/m^3 Cr^{VI} are supposed to be associated with risks of 7 x 10^{-2} and 1.4 x 10^{-3}.

Furthermore the Dutch expert committee on occupational standards calculated risk estimates for chromium (VI) [Health Council of the Netherlands 1998]. Likewise these estimates were mainly based on the study from Mancuso [1975] and evaluations from US-EPA [US-EPA, 1984]. The committee considers all chromium (VI) compounds to be carcinogenic in humans. A genotoxic mode of action is assumed and the committee has no reason to deviate from the method of a linear exposure response relationship for these compounds. Additional cancer risks of 4 x 10^{-3} and 4 x 10^{-5} were estimated for a long-term occupational chromium (VI) exposure to 2 µg/m^3 and 0.02 µg/m^3 Cr^{VI}, respectively.

The Scientific Committee on Occupational Exposure Limits [SCOEL 2004] issued a risk assessment on hexavalent chromium which also includes quantitative risk estimates. It is based on a summary of ten published studies [Steenland et al., 1996] and refers to soluble and insoluble chromium (VI) compounds. In addition it is mentioned that an increased potency of soluble salts compared to insoluble salts is possible. The number of excess lung cancers per 1000 workers has been estimated to be 2 - 14 for an exposure level of 25 µg/m^3, 1 - 6 for an exposure level of 10 µg/m^3, 0.5 - 3 for an exposure level of 5 µg/m^3 and 0.1 - 0.6 for an exposure level of 1 µg/m^3 Cr^{VI}.

According to SCOEL [2004] a risk assessment for hexavalent chromium was also prepared for the US Occupational Safety and Health Administration (OSHA) [Crump, 1995]. Based on the data from Mancuso [1975] 6 - 9 excess lung cancer deaths per 1000 workers were predicted for an occupational long-term exposure to 1 µg/m^3 of chromium (VI). In a second approach the study of Hayes et al. [1979] was taken as the central basis resulting in 2 excess lung cancer deaths per 1000 for an exposure level of 1 µg/m^3 Cr^{VI}.

A further risk estimate was developed by NIOSH [2008] for all chromium (VI) compounds. Based on the study of Park et al. [2004] NIOSH estimated an excess risk of lung cancer death of about one per 1000 workers for an exposure of 0.2 µg /m^3 Cr^{VI}.

To compare the risk estimates the risks associated to an exposure of 1 µg/m^3 Cr^{VI} and a long term occupational exposure are summarized in table 21.

Table 21: Excess lung cancer cases per 1000 associated to an exposure of 1 µg/m^3 Cr^{VI}

Author	Excess lung cancer cases per 1000
SCOEL 2004 [Steenland et al., 1996]	0.1 – 0.6
EC 2005 Annex H [US-EPA 1998a, US-EPA 1998b, Mancuso, 1975, Mancuso, 1997]	1.4
Health council of the Netherlands 1998 [US-EPA 1984, Mancuso 1975]	2
Crump 1995 for US-OSHA [Hayes, 1979] (cited in SCOEL 2004)	2
NIOSH 2008 [Park et al., 2004]	5
Crump 1995 for US-OSHA [Mancuso, 1975] (cited in SCOEL 2004)	6 – 9

Interestingly, the majority of authors and institutions calculate risks in the same order of magnitude. Only the estimate of SCOEL [2004] is one order of magnitude lower than the others. The different values can be explained by differences concerning the used data basis, the assumptions introduced and the methods of statistics and risk prediction.

Finally all risk estimates have in common that chromium (VI) is assumed to be a non-threshold carcinogen with the consequence of a non-threshold approach to calculate risks. For details see the cited literature.

The estimates from the European institutions are of special importance [EC, 2005; SCOEL, 2004]. In addition, the NIOSH-estimate is considered to be of special value, because it considers more recent information.

What risk level should be considered as acceptable or tolerable for occupational settings has not been harmonised on a European scale, but national approaches have been developed. In Germany, for example, an additional risk of 4 : 1000 is considered as tolerable, while a risk of 4 : 10000 is considered as acceptable for the time being. For 2018, a lowered acceptable risk of 4 : 100000 is envisaged [AGS, 2008]. Comparing these normative benchmarks for decision making with the range of risk estimates, exemplified by those of SCOEL [2004], EC [2005] and NIOSH [2008], tentative tolerable and acceptable exposure concentrations can be calculated (Table 22). Approximate values for a tolerable concentration would range from 1 to 40 µg/m^3 Cr^{VI}, those for an acceptable exposure concentration from 0.1 to 4 µg/m^3 Cr^{VI} and those for an acceptable exposure concentration envisaged for 2018 from 0.01 to 0.4 µg/m^3 Cr^{VI}.

Table 22: Derivation of approximate tolerable and acceptable exposure concentrations of hexavalent chromium by combination of risk estimates (SCOEL, NIOSH) with benchmarks for decision making currently in use in Germany

Author of risk estimate	Tolerable exposure concentration, risk: 4:1000 (in µg/m^3 Cr^{VI})	Acceptable exposure concentration, risk: 4:10000 (in µg/m^3 Cr^{VI})	Acceptable exposure concentration 2018, risk: 4:100000 (in µg/m^3 Cr^{VI})
SCOEL [2004]	**7 - 40**	**0.7 - 4**	**0.07 - 0.4**
EC [2005]	**3**	**0.3**	**0.03**
NIOSH [2008]	**1**	**0.1**	**0.01**

The diversity of uses of chromium trioxide is presented and discussed in chapter 2 in detail. A selection of occupational exposure measurements is displayed in figure 1 to 4 and compared with the risk estimates of SCOEL [2004], EC [2005] and NIOSH [2008]. In figure 1 for example an overview is given about metal working & mechanical engineering, which represents the most important scenario. About 75 % of the production volume is used there. Furthermore about 80 % of measurement values originate from metal working & mechanical engineering. It becomes apparent in figure 1 that the distributions of measurements, sorted by personal or static measurement or the use of LEV, are comparable. The 90th percentile values for example are all close to 10 µg Cr^{VI} which would be associated to 1 – 50 excess lung cancer cases per 1000, pending on the risk estimates applied (SCOEL [2004], EC [2005] and NIOSH [2008]). At least in Germany this would partly exceed the tolerable exposure concentration, which already considers to some extent economic needs and should be kept anyway. An acceptable exposure, which is one order of magnitude lower and defined as health based exposure limit concentration is clearly exceeded.

As presented above inhalation represents an important route of occupational exposure, but dermal exposure has to be considered in addition. Concerning dermal exposure the skin sensitising property of hexavalent chromium is a major problem at workplaces. Thus the mitigation and control of dermal exposure is of special concern for risk management.

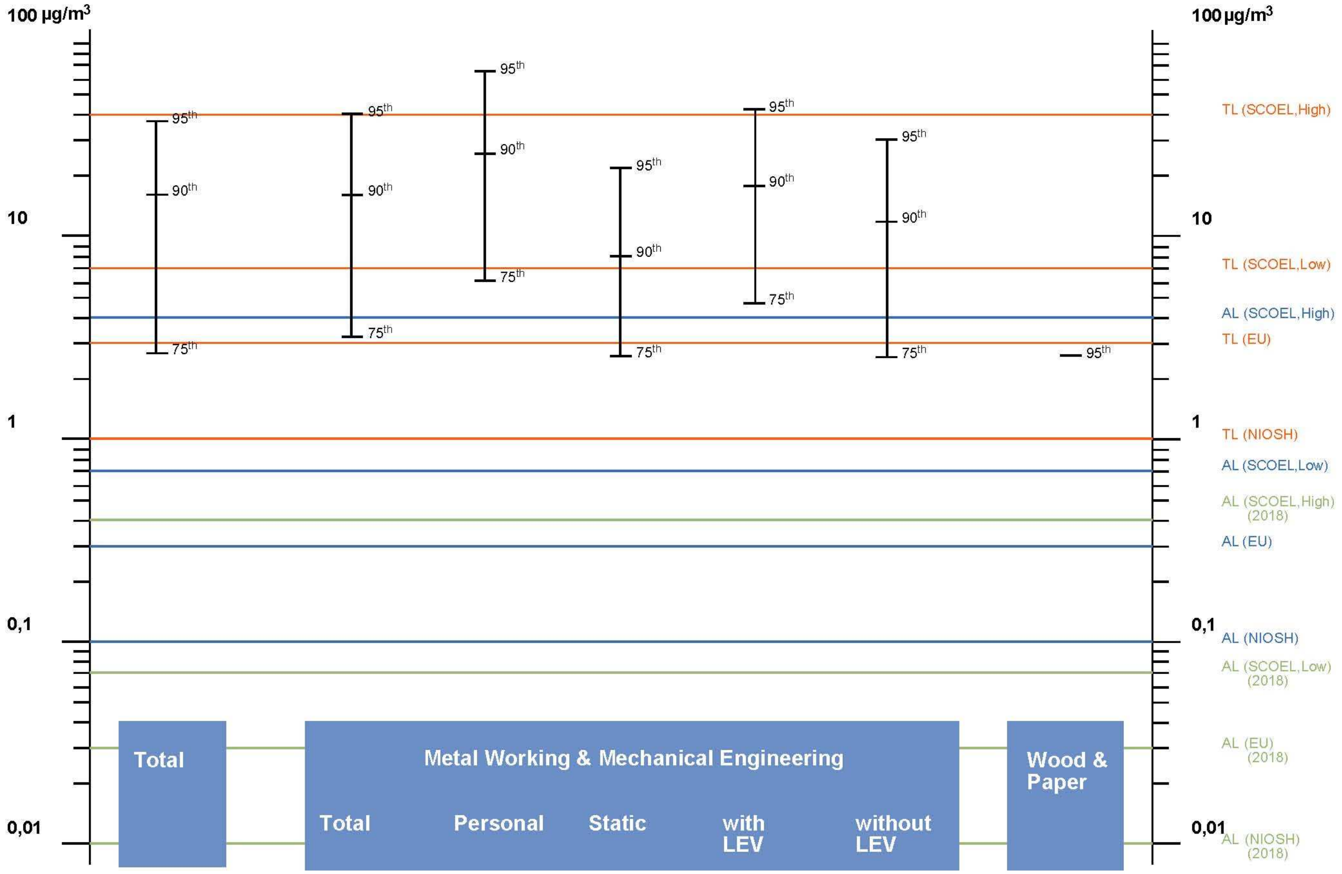

Figure 2: Overview on inhalative exposure data (measurements) in the main branches (Total; Metal Working & Mechanical Engineering; Wood & Paper) in relation to risk estimates combined with German proposals of tolerable (TL) or acceptable (AL) risk levels.

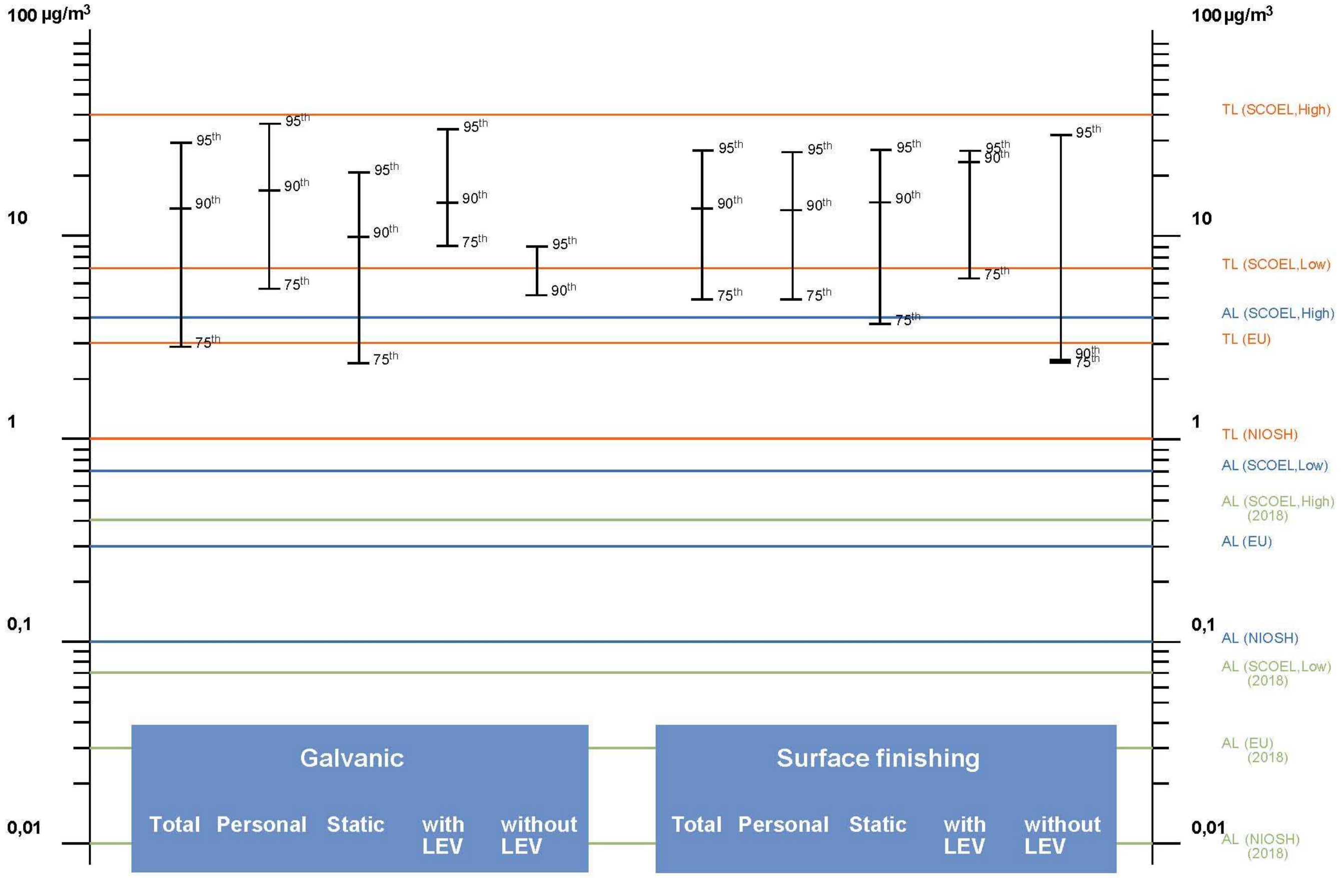

Figure 3: Detailed inhalative exposure data (measurements) in metal working and mechanical engineering in relation to risk estimates combined with German proposals of tolerable (TL) or acceptable (AL) risk levels.

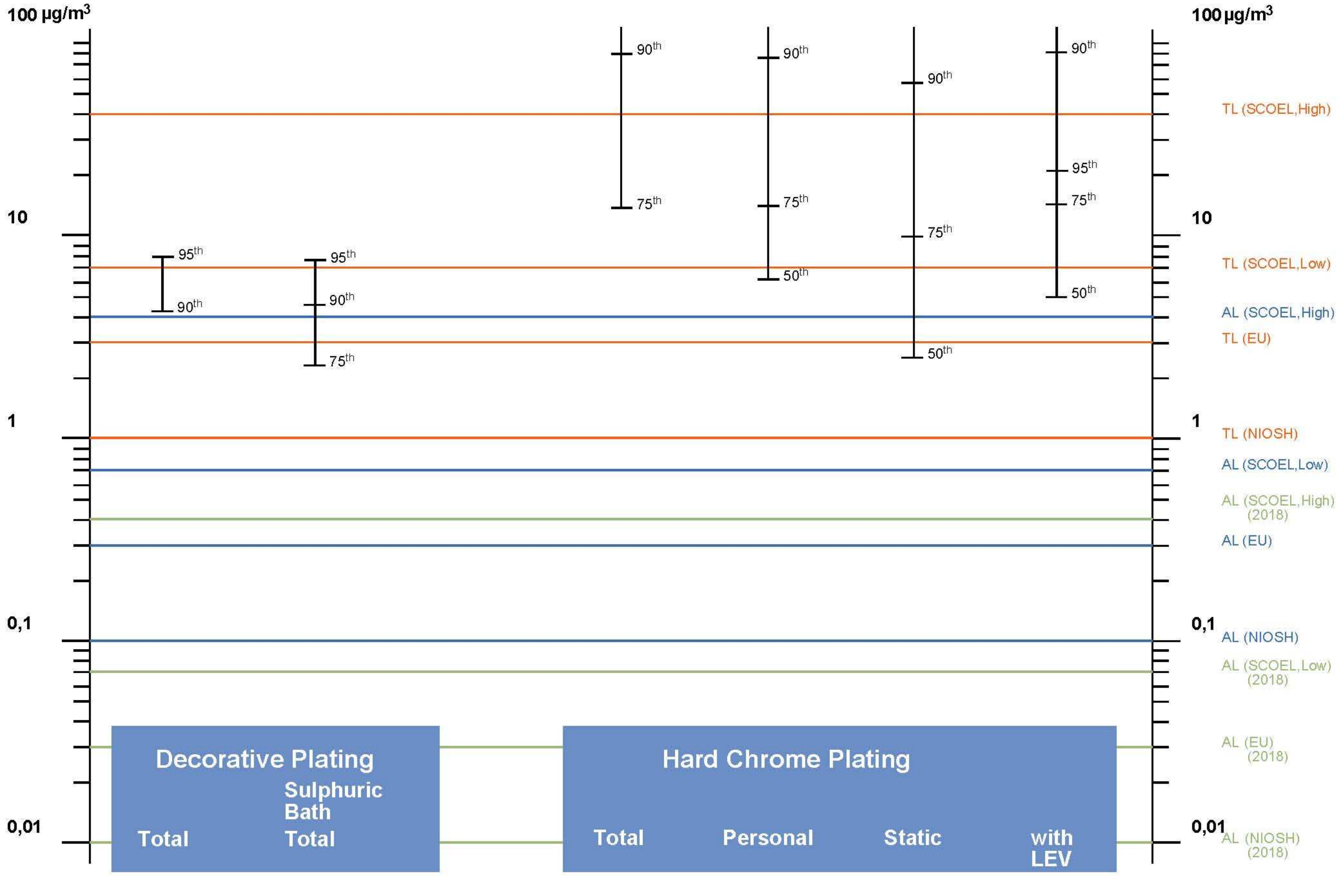

Figure 4: Inhalative exposure data for the uses Decorative Plating and Hard Chrome Plating in relation to risk estimates combined with German proposals of tolerable (TL) or acceptable (AL) risk levels.

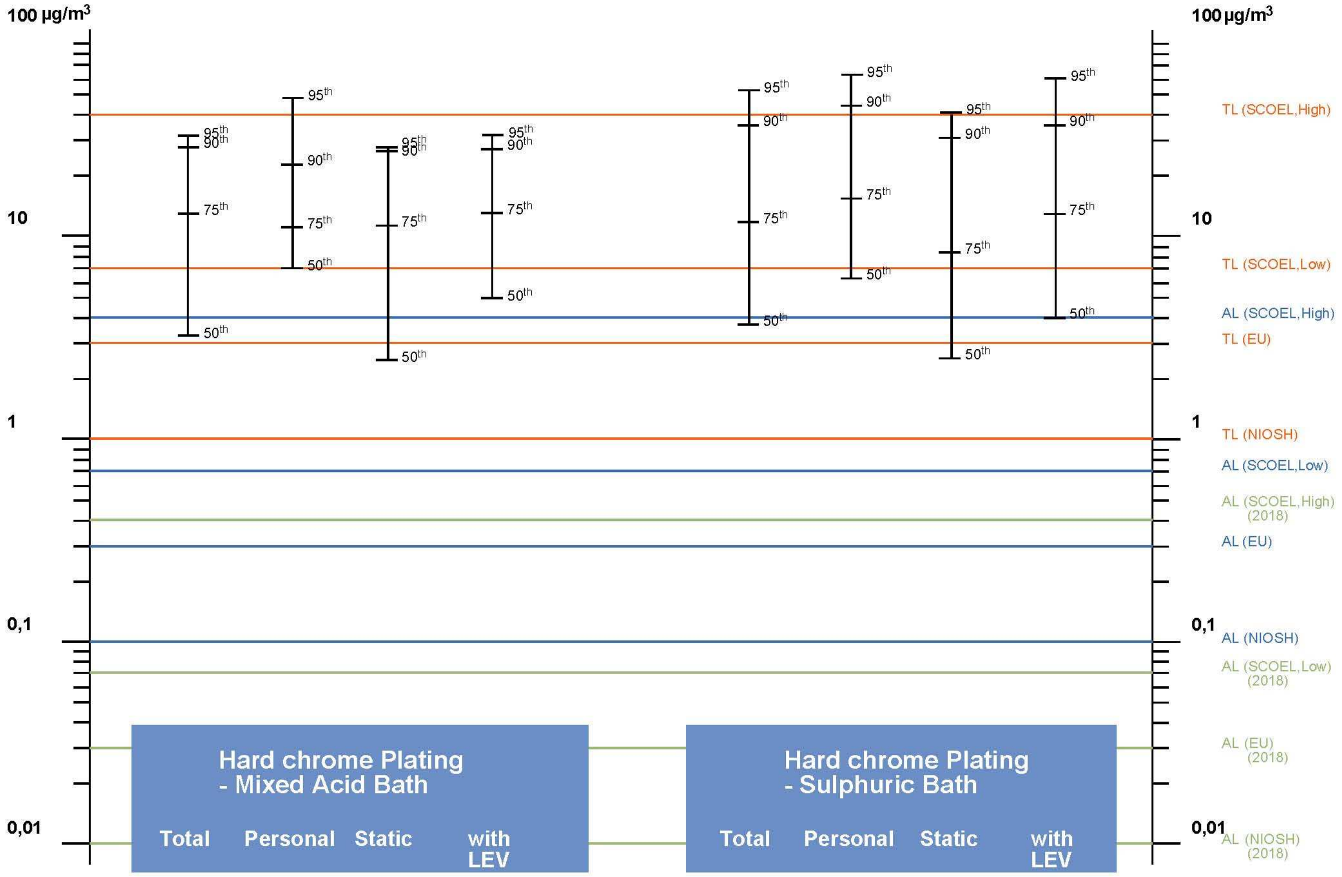

Figure 5: Detailed inhalative exposure data for the use Hard Chrome Plating in relation to risk estimates combined with German proposals of tolerable (TL) or acceptable (AL) risk levels.

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ABBREVIATIONS

ACQ	alkaline Copper quaternary ammonium compound
AFRL	Air Force Research Laboratory
AGS	(German) Committee on Hazardous Substances
APU	Auxiliary Power Unit
Arithm. Central	Arithmetic Mean
ATSDR	Agency For Toxic Substances And Disease Registry
BG/BGIA	(German) employer's liability insurance association / Institute for Occupational Safety and Health
BGMG	BG Measurement System for Hazardous Substances (now: MGU)
BIA	Institute for Occupational Safety and Health of the German Social Accident Insurance (now: IFA)
BMWi	German Federal Ministry of Economics and Technology
C & L	Classification and Labelling
CC	Copper Chrome
CCA	Copper Chrome Arsenate
CCB	Copper Chrome Boron
CCC	Chromate Conversion Coating
CCP	Copper Chrome Phosphate
CMR	Carcinogen, Mutagen, toxic for Reproduction
CVD	Chemical Vapor Deposition
DEFRA	Department for Environment, Food and Rural Affairs, UK
DIN EN ISO	German Institute for Standardization
DLC	Diamond-Like Carbon
DNEL(s)	Derived No Effect Level(s)
EASE	Estimation and Assessment of Substance Exposure
EC	European Community
ECCS	Electrolytic Chromium/Chromium oxide Coated Steel
ECHA	European Chemicals Agency
EEC	European Economic Community
ELV	End-of-Life Vehicles
EN 10202	European Norm 10202
EU	European Union
Geom	Geometric mean
GSD	Geometric standard deviation

HSE	Health and Safety Executive, UK
HVOF	High Velocity Oxy Fuel
IARC	International Agency on the Research on Cancer
IBD	primary ion beam deposition of carbon ions
ICDA	International Chromium Development Association
ID	Internal Diameter
IFA	Institute for Occupational Safety and Health of the German Social Accident Insurance
LEV	Local Exhaust Ventilation
LOQ	Limit of Quantification
MEGA PRO	developed software MEGA
MEGA	measurement data to exposure to hazardous substances at work
MGU	Messsystem Gefährdungsermittlung der Unfallversicherungsträger (formerly: BGMG)
MKS	Micro-layer corrosion protection system
n/a	not applicable
NIOSH	National Institute of Occupational Safety and Health
O & R	Overhaul and Repair
OEM	Original Equipment Manufacturing
OSHA	US Occupational Safety and Health Assocciation
PACVD	Plasma Assisted Chemical Vapour Deposition
PBT	Persistent, bioaccumulative and toxic
PEL	Permissible Exposure Limit
Perc.	Percentile
PNEC	Predicted No Effect Concentration
PTFE	Polytetrafluorethan
PVD	Physical Vapor Deposition
R & D	Research and Development
RAR	Risk Assessment Report
REACH	Registration, Evaluation and Authorization of Chemicals
RF	Radio frequency
RoHS	Restriction Of the use of certain Hazardous Substances in electrical and electronic equipment
RRS	Risk Reduction Strategy
RWC	Reasonable Worst-Case
SCOEL	Scientific Committee on Occupatonal Exposure Limits

SMEs	Small or Medium Enterprises
Std Dev.	Standard Deviation
SVHC	Substance of Very High Concern
TDG	Thermal Diffusion Galvanizing
US EPA	US Environment Protection Agency
USDA	US Department of Agriculture
WC	Tungsten Carbide
VDMA	Verband Deutscher Maschinen- und Anlagenbau e.V.
VHN	Vickers Hardness Number
vPvB	very Pollutant, very Biopersistent